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(71) Applicant: NKK CORPORATION
Tokyo 100 (JP)

(72) Inventors:
• Urakawa, Takayuki,
NKK Corp.
Kawasaki-ku, Kawasaki 210 (JP)
• Imokawa, Toru,
NKK Corp.
Kawasaki-ku, Kawasaki 210 (JP)

- Sakurai, Michitaka,
NKK Corp.
Kawasaki-ku, Kawasaki 210 (JP)
- Inagaki, Jun-ichi,
NKK Corp.
Kawasaki-ku, Kawasaki 210 (JP)
- Yamashita, Masaaki,
NKK Corp.
Kawasaki-ku, Kawasaki 210 (JP)
- Nomura, Shuji,
NKK Corp.
Kawasaki-ku, Kawasaki 210 (JP)

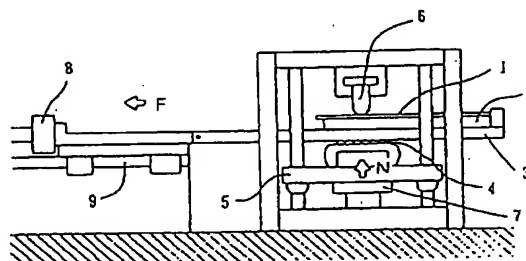
(74) Representative: Hansen, Bernd, Dr. Dipl.-Chem.
et al
Hoffmann, Eitle & Partner,
Patentanwälte,
Arabellastrasse 4
81925 München (DE)

(54) Zinciferous plated steel sheet and method for manufacturing same

(57) A method for manufacturing a zinciferous plated steel sheet, comprises: forming a zinciferous plating layer on a steel sheet; and forming an Fe-Ni-O film on the zinciferous plating layer. The Fe-Ni-O film is formed by carrying out electrolysis with the steel sheet

as a cathode in an aqueous solution, dipping the steel sheet in an aqueous solution, or spraying a mist on a surface of the zinciferous plating layer.

FIG. 1



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Description

BACKGROUND OF THE INVENTION

1. Field of the Invention

The present invention relates to a zinciferous plated steel sheet, and more particularly, to a zinciferous plated steel sheet excellent in press formability, spot weldability, and adhesiveness, and a method for manufacturing same.

2. Description of the Related Arts

Zinciferous plated steel sheets are widely applied as various rust-prevention steel sheets because of many excellent properties. In order to use the zinciferous plated steel sheets as rust-preventive steel sheets for automobile, it is important for the sheets to be excellent in press formability, spot weldability and adhesiveness as properties required in the body forming process, in addition to corrosion resistance and painting adaptability.

In general, however, the zinciferous plated steel sheet has a defect of being inferior to a cold-rolled steel sheet in press formability. This is attributable to a larger sliding resistance between the zinciferous plated steel sheet and a press die than that for the cold-rolled steel sheet: a larger sliding resistance makes it difficult for the portion of the zinciferous plated steel sheet near the bead portion of the die to flow into the press die, leading to easier occurrence of fracture of the steel sheet.

For the purpose of improving press formability of the zinciferous plated steel sheet, a method of applying a high-viscosity lubricant is commonly employed. This method however involves problems of occurrence of a painting defect caused by defective degreasing in the painting process which follows due to the high viscosity of lubricant, and press properties becoming unstable as a result of lubricant shortage. There is therefore an increasing demand for improvement of press formability of the zinciferous plated steel sheet.

In the zinciferous plated steel sheet, on the other hand, a brittle alloy layer is easily formed through reaction between a copper electrode and molten zinc during spot welding. This results in serious wear of the copper electrode, leading to a short service life, and hence to a problem of an inferior continuous spot weldability as compared with the cold-rolled steel sheet.

In the manufacturing process of an automobile body, furthermore, various adhesives are used for rust prevention and inhibition of vibration. An inferior adhesiveness of the zinciferous plated steel sheet to that of the cold-rolled steel sheet has recently been clarified.

As a method for solving these problems, Japanese Unexamined Patent Publications No. 53-60,332 and No. 2-190,483 disclose a method of improving weldability or workability, through forming of an oxide film mainly comprising ZnO, by applying an electrolytic treatment, a dipping treatment, a coating/oxidation treatment or a heat treatment onto the surface of the zinciferous plated steel sheet (hereinafter referred to as the "prior art 1").

Japanese Unexamined Patent Publication No. 4-88,196 discloses a method of improving press formability and chemical treatability through forming of an oxide film mainly comprising P oxide on the surface of a zinciferous plated steel sheet by dipping the plated steel sheet in an aqueous solution having a pH of from 2 to 6 containing from 5 to 60 g/l sodium phosphate, or by electrolysis, or by sprinkling said aqueous solution (hereinafter referred to as the "prior art 2").

Japanese Unexamined Patent Publication No. 3-191,093 discloses a method of improving press formability and chemical treatability by forming Ni oxide (hereinafter referred to as the "prior art 3"), and Japanese Unexamined Patent Publication No. 58-67,885 discloses a method of improving corrosion resistance by forming a metal such as Ni and Fe through electroplating or chemical plating which is not limitative on the surface of a zinciferous plated steel sheet (hereinafter referred to as the "prior art 4").

The foregoing prior art 1 involves the following problem. This prior art, which is a method of forming an oxide film mainly comprising ZnO on the surface of the plating layer by any of various treatments, provides only a limited effect of reducing sliding resistance between the press die and the plated steel sheet, resulting in a limited effect of improving press formability. The oxide film mainly comprising ZnO causes deterioration of adhesiveness.

The prior art 2, which is a method of forming an oxide film mainly comprising P oxide on the surface of a zinciferous plated steel sheet, while providing a remarkable improvement effect of press formability and chemical treatability, has a drawback of causing deterioration of spot weldability and adhesiveness.

The prior art 3, which forms a film comprising a single phase of Ni oxide, has a problem of deterioration of adhesiveness, although it permits improvement of press formability.

The prior art 4, which is a method of forming only metals such as Ni, improves corrosion resistance. The improving effect of press formability and spot weldability is not however sufficient because of strong metallic properties of the film, and a low wettability of metals relative to an adhesive makes it unavailable a sufficient adhesiveness.

SUMMARY OF THE INVENTION

It is an object of the present invention to provide a zinciferous plated steel sheet excellent in press formability, spot weldability and adhesiveness, and a method for manufacturing same.

To attain the object, the present invention provides a method for manufacturing a zinciferous plated steel sheet, comprising the steps of: forming a zinciferous plating layer on a steel sheet; and forming an Fe-Ni-O film on the zinciferous plating layer.

First, said step of forming the Fe-Ni-O film can comprise carrying out electrolysis with the steel sheet, on which the zinciferous plating layer is formed, as a cathode in an aqueous solution containing nickel sulfate, ferrous sulfate and ferric sulfate. The aqueous solution has a total concentration of the nickel sulfate, the ferrous sulfate and the ferric sulfate, a ratio of concentration (mol/l) of an Fe^{3+} to a sum of concentration of an Fe^{2+} and the Fe^{3+} and a pH, said total concentration is within a range of from 0.3 to 2 mol/l, said ratio of concentration (mol/l) is within a range of from 0.5 to less than 1.0, and a pH is within a range of from 1 to 2.

Secondly, the step of forming the Fe-Ni-O film can comprise carrying out electrolysis with the steel sheet, on which the zinciferous plating layer is formed, as a cathode in a plating solution containing nickel sulfate and ferrous sulfate. The plating solution has a total concentration of the nickel sulfate and the ferrous sulfate and a pH, the total concentration is within a range of from 0.1 to 2 mol/l and the pH is within a range of from 1 to 3. The electrolysis is carried out on conditions satisfying the following equation:

$$50 \leq I_K / (U^{1/2} \cdot M) \leq 150$$

where M represents a sum of the concentrations (mol/l) of nickel ions and ferrous ions in the plating solution; U represents a mean flow rate (m/s) of the plating solution; and I_K represents a current density (A/dm^2) in the electrolysis.

Thirdly, the step of forming the Fe-Ni-O film can comprise dipping the steel sheet, on which the zinciferous plating layer is formed, in an aqueous solution containing at least one of ferrous sulfate and ferrous nitrate and at least one of nickel sulfate and nickel nitrate. A sum of an iron content (mol/l) and a nickel content (mol/l) in the aqueous solution is within a range of from 0.1 to 3.0 mol/l, a ratio of the iron content (mol/l) to the sum of the iron content (mol/l) and the nickel content (mol/l) in the aqueous solution is within a range of from 0.004 to 0.9, pH is within a range of from 1.0 to 3.5, and temperature is within a range of from 20 to 70 °C.

Fourthly, the step of forming the Fe-Ni-O film can be performed after treating the steel sheet, on which the zinciferous plating layer is formed, in an alkaline solution having a pH of at least 10 for a period within a range of from 2 to 30 seconds. The step of forming the Fe-Ni-O film can comprise treating the steel sheet, on which the zinciferous plating layer is formed, in an aqueous solution containing FeCl_2 and NiCl_2 and having a pH within a range of from 2.0 to 3.5 and a temperature within a range of from 20 to 70 °C. The step of forming the Fe-Ni-O film can comprise treating the steel sheet, on which the zinciferous plating layer is formed, in an aqueous solution containing FeCl_2 and NiCl_2 and having a pH within a range of from 2.0 to 3.5, a temperature within a range of from 20 to 70 °C, and a ratio of Fe content (wt.%) to the sum of the Fe content (wt.%) and a Ni content (wt.%) being within a range of from 0.004 to 0.9.

Fifthly, the step of forming the Fe-Ni-O film can comprise: spraying a mist solution containing Fe ions and Ni ions and having pH of 1 to 3.5 on a surface of the zinciferous plating layer which is formed on the steel sheet; maintaining the steel sheet at a temperature of 20 to 70 °C for 1 second or more; and heating the steel sheet. Thereby the Fe-Ni-O film having a coating weight within the range of 10 to 1500 mg/m^2 in terms of the total weight of the metallic elements, a rate of coating within the range of 30 to 90%, and an island-like or mosaic distribution is formed on the zinciferous plating layer.

Sixthly, the step of forming the Fe-Ni-O film can comprise: temper rolling the steel sheet, on which the zinciferous plating layer is formed, to form fine irregularities on the zinciferous plating layer; and forming the Fe-Ni-O film on the zinciferous plating layer. Thereby the Fe-Ni-O film having a coating weight within the range of 10 to 1500 mg/m^2 in terms of the total weight of the metallic elements, a rate of coating within the range of 30 to 90%, and an island-like or mosaic distribution is formed on the zinciferous plating layer.

Seventhly, said step of forming the Fe-Ni-O film can comprise: temper rolling the steel sheet, on which the zinciferous plating layer is formed, to form a new surface on the zinciferous plating layer; and forming the Fe-Ni-O film on the zinciferous plating layer. Thereby the Fe-Ni-O film having a coating weight within the range of 10 to 1500 mg/m^2 in terms of the total weight of the metallic elements, a rate of coating within the range of 30 to 90%, and an island-like or mosaic distribution is formed on the zinciferous plating layer.

Eighthly, said step of forming the Fe-Ni-O film can comprise: dipping the steel sheet, on which the zinciferous plating layer is formed, in an acid solution or an alkaline solution to dissolve an air oxide film existing on a surface of the zinciferous plating layer and to form active and inactive portions on the surface of the zinciferous plating layer; and forming the Fe-Ni-O film on the zinciferous plating layer on which the active and inactive portions are formed.

Ninthly, said step of forming the Fe-Ni-O film can comprise: performing an anodic electrolysis in an acid solution or an alkaline solution to the steel sheet, on which the zinciferous plating layer is formed, to dissolve an air oxide film exist-

ing on a surface of the zinciferous plating layer and to form active and inactive portions on the surface of the zinciferous plating layer; and forming the Fe-Ni-O film on the zinciferous plating layer on which the active and inactive portions are formed.

Tenthly, said step of forming the Fe-Ni-O film can comprise: temper rolling the steel sheet, on which the zinciferous plating layer is formed, within the range of an elongation rate of 0.3 to 5.0 %; performing an alkali treatment to the temper-rolled steel sheet in an alkaline solution having a pH of 10 or more for the period of 2 to 30 seconds; and forming the Fe-Ni-O film on the surface of the zinciferous plating layer for which the alkali treatment is performed.

Eleventhly, said step of forming the Fe-Ni-O film can comprise: performing an alkali treatment to the steel sheet, on which the zinciferous plating layer is formed, in an alkaline solution having a pH of 10 or more for the period of 2 to 30 seconds; temper rolling the steel sheet, for which the alkali treatment is performed, within the range of an elongation rate of 0.3 to 5.0 %; and forming the Fe-Ni-O film on the surface of the plating layer of the temper rolled steel sheet.

Further, the present invention provides a zinciferous plated steel sheet comprising: a steel sheet; a zinciferous plating layer which is formed on the steel sheet; and an Fe-Ni-O film which is formed on the zinciferous plating layer.

The Fe-Ni-O film has an island-like or mosaic form, a coating weight within the range of 10 to 1500 mg/m² in terms of the total weight of metallic elements in the Fe-Ni-O film, and a rate of surface coating within the range of 30 to 90%.

The zinciferous plating layer is an alloyed zinc dip-plating layer, and said alloyed zinc dip-plating layer comprises 6 to 11 wt. % Fe and the balance being Zn and inevitable and has a coating weight of 20 to 100 g/m². The Fe-Ni-O film is formed on the surface of the alloyed zinc dip-plating layer. Said Fe-Ni-O film has a coating weight within the range of 10 to 1500 mg/m² in terms of the total weight of metallic elements in the Fe-Ni-O film; and a ratio of the Fe content (wt%) to the total of the Fe content (wt%) and a Ni content (wt%) which is within the range of 0.004 to 0.9; and an oxygen content which is within the range of 0.5 to 10 wt%.

The zinciferous plating layer is an alloyed zinc dip-plating layer; said alloyed zinc dip-plating layer comprises 9 to 14 wt. % Fe and the balance being Zn and inevitable, and has a surface alloy phase which is 81 alloy phase and a coating weight of 20 to 100 g/m². The Fe-Ni-O film is formed on the surface of the alloyed zinc dip-plating layer. Said Fe-Ni-O film has a coating weight within the range of 10 to 1500 mg/m² in terms of the total weight of metallic elements in the Fe-Ni-O film; and a ratio of the Fe content (wt%) to the total of the Fe content (wt%) and a Ni content (wt%) which is within the range of 0.004 to 0.9; and an oxygen content which is within the range of 0.5 to 10 wt%.

BRIEF DESCRIPTION OF THE DRAWINGS

FIG. 1 is a schematic front view of a frictional coefficient measuring apparatus.

FIG. 2 is a schematic perspective view illustrating the shape and size of a first type bead (bead type A) shown in Fig. 1.

FIG. 3 is a schematic perspective view illustrating the shape and size of a second type bead (bead type B) shown in Fig. 1.

FIG. 4 is a schematic perspective view illustrating a process of assembly of a test piece for adhesiveness test.

FIG. 5 is a schematic perspective view illustrating loading of a tensile load upon measuring peeloff strength in an adhesiveness test.

FIG. 6 is a graph illustrating an example of the relationship between the coating weight of Ni and frictional coefficient in a zinciferous plated steel sheet in cases with and without an alkali treatment.

FIG. 7 is a graph illustrating differences in coating weight of Ni among cases with immersion in a chloride bath, a sulfate bath and nitrate bath as an Fe-Ni-O film forming treatment solution.

FIG. 8 is a graph illustrating an example of coating weight of Ni relative to the dipping time at various values of pH.

FIG. 9 is a schematic drawing illustrating a longitudinal section of a zinciferous plated steel sheet in accordance with an embodiment of the present invention.

FIG. 10 is a schematic drawing illustrating a longitudinal section of a zinciferous plated steel sheet in accordance with an embodiment of the present invention in which the zinciferous plated steel sheet is temper-rolled by using a rolling roll having a surface with fine irregularities formed therein, and then treated to form a Fe-Ni-O film.

FIG. 11 is a schematic drawing illustrating a longitudinal section of a zinciferous plated steel sheet in accordance with an embodiment of the present invention in which the zinciferous plated steel sheet is temper-rolled by using a rolling roll having a relatively smooth surface, and then treated to form a Fe-Ni-O film.

FIG. 12 is a schematic drawing illustrating a longitudinal section of a zinciferous plated steel sheet in accordance with an embodiment of the present invention in which an air oxide film on the surface of the zinciferous plated steel sheet is partly dissolved by dipping in an acid solution or anodic electrolysis in an acid solution to form active and inactive portions in the deposit surface.

FIG. 13 is a schematic perspective view illustrating the method of evaluating the adhesiveness between a chemically treated film and a zinciferous plating layer itself, which is a characteristic of a zinciferous plated steel sheet of the present invention.

FIG. 14 is a graph which shows by way of example the relationship between a coating weight of Ni to a zinciferous

plated steel sheet and frictional coefficient in the case that alkali solution treatment and temper rolling are performed for the steel sheet as well as the case that the foregoing treatments are not performed.

FIG. 15 is a graph which shows the difference in coating weight of Ni to the zinciferous plated steel sheet in the case that it is dipped in a chloride bath, a sulfate bath and a nitrite bath serving as a treatment liquid for Fe-Ni-O film.

FIG. 16 is a graph which shows by way of example a coating weight of Ni to the zinciferous plated steel sheet relative to the dipping time in the case that pH is changed.

FIG. 17 is a schematic perspective view showing a specimen after being subjected to a cup deep drawing test.

FIG. 18 a cross-sectional view, shown schematically and vertically, of a draw bead testing machine used for examination of powdering resistance.

FIG. 19 is a partly enlarged view of Figure 4.

FIG. 20 is a view explanatory of the shape and dimension of a bead tip.

DESCRIPTION OF THE EMBODIMENT

EMBODIMENT 1

The present inventors carried out extensive studies to solve the above-mentioned problems, and found the possibility of largely improving press formability, spot weldability and adhesiveness by forming an appropriate Fe-Ni-O film on the surface of a plating layer of a zinciferous plated steel sheet.

The findings thus obtained reveal that the appropriate Fe-Ni-O film should satisfy the following conditions (1) to (3):

- (1) The coating weight of the film is within a range of from 10 to 1,500 mg/m²;
- (2) The ratio of Fe content (wt.%) to the total content of Fe and Ni (wt.%) in this film (hereinafter referred to as the "Fe ratio in film" and expressed as $\text{Fe} / (\text{Fe} + \text{Ni})$) is within a range of from 0.05 to 0.9, or more preferably, from 0.1 to 0.5; and
- (3) The oxygen content in this film is within a range of from 0.5 to 10 wt.%.

The zinciferous plated steel sheet is inferior to the cold-rolled steel sheet in press formability because, under a high surface pressure, zinc having a low melting point sticks to the die, leading to an increase in sliding resistance. In order to avoid this inconvenience, it is effective to form a film having a higher hardness and a higher melting point than a zinc or zinc alloy plating layer on the surface of the plating layer of the zinciferous plated steel sheet, which reduces sliding resistance between the surface of the plating layer and the press die during press forming, and enables the zinciferous plated steel sheet to more easily slip into the press die, thus improving press formability.

The zinciferous plated steel sheet is inferior to the cold-rolled steel sheet in continuous spot weldability because, during welding, molten zinc comes into contact with the copper electrode and forms a brittle alloy layer which causes a more serious deterioration of the electrode. A method of forming a film having a high melting point on the surface of the plating layer is believed to be effective for the purpose of improving continuous spot weldability. To improve spot weldability of the zinciferous plated steel sheet, the present inventors found it particularly effective to use Ni metal as a result of studies on various films. Although the reason is not clear, conceivable causes are the high melting point and the high electric conductivity of Ni metal.

While the zinciferous plated steel sheet has been known to be inferior to the cold-rolled steel sheet in adhesiveness, the cause has not as yet been clarified. As a result of studies on the cause of this inferiority, the present inventors elucidated that adhesiveness was governed by the chemical composition of the oxide film on the surface of the zinciferous plating layer. More specifically, while the oxide film on the surface of the cold-rolled steel sheet mainly comprises Fe oxide, the film on the surface of the zinciferous plating layer mainly comprises Zn oxide. Adhesiveness varies with the chemical composition of the oxide film: Zn oxide are inferior to Fe oxide in adhesiveness. It is now possible therefore to improve adhesiveness by forming a film containing Fe oxide on the surface of the zinciferous plated steel sheet, as in the present invention.

The present invention was developed on the basis of the findings as described above, and provides a method of manufacturing a zinciferous plated steel sheet excellent in press formability, spot weldability and adhesiveness by appropriately forming an Fe-Ni-O film on the surface of a plating layer of the zinciferous plated steel sheet.

It suffices that the Fe-Ni-O film has a microscopic structure and a form such that the film comprises a mixture containing at least Ni and Fe metals and oxides of Ni and Fe, irrespective of the binding condition of elements constituting the film.

The method of manufacturing a zinciferous plated steel sheet in Embodiment 1 is characterized in that it comprises the step of carrying out electrolysis with a zinciferous plated steel sheet as a cathode in an aqueous solution containing nickel sulfate, ferrous sulfate and ferric sulfate, thereby forming a film on a surface of a plating layer of the zinciferous plated steel sheet, wherein an Fe-Ni-O film is formed by conducting electrolysis in the aqueous solution in which the total concentration of nickel sulfate, ferrous sulfate and ferric sulfate is within a range of from 0.3 to 2.0 mol/l, the ratio

of concentration (mol/l) of Fe^{3+} to the sum of concentration of Fe^{2+} and Fe^{3+} is within a range of from 0.5 to under 1.0, and pH is from 1.0 to 2.0. The plating layer of the zinciferous plated steel sheet can be an alloyed dip-plating layer having an iron content within a range of from 7 to 15 wt.%. The plating layer of the zinciferous plated steel sheet can be a zinc electroplating layer or a zinc dip-plating layer.

In the present invention, nickel sulfate, ferrous sulfate and ferric sulfate are used as components of the aqueous solution for forming an Fe-Ni-O film on the surface of a plating layer of the zinciferous plated steel sheet (hereinafter referred to as the "electrolytic solution") because electrolysis carried out with the zinciferous plated steel sheet to have the Fe-Ni-O film formed thereon as the cathode is suitable for forming the film effectively containing Fe, Ni and O.

The total concentration of nickel sulfate, ferrous sulfate and ferric sulfate should be within a range of from 0.3 to 2.0 mol/l for the following reason.

If the total concentration of these three chemical components is under 0.3 mol/l, the low electric conductivity of the electrolytic bath results in a higher electrolytic voltage. Even with a low current density, therefore, plating burn proceeds too far so that the oxygen content in the Fe-Ni-O film exceeds 10 wt.%, thus easily causing a decrease in spot weldability and chemical treatability.

With a total concentration of these components of over 2.0 mol/l, on the other hand, at a low temperature, the limit of solubility of nickel sulfate and/or ferrous sulfate is reached, thus causing precipitation of nickel sulfate and/or ferrous sulfate.

An aqueous solution having a pH of within a range of from 1.0 to 2.0 is used as the electrolytic solution for the following reason.

With a pH of the electrolytic solution of under 1.0, hydrogenation plays a main role in the cathodic reactions during electrolysis, leading to a large decrease in the current efficiency. With a pH of the electrolytic solution of over 2, on the other hand, ferric hydroxide is precipitated.

The ratio of Fe^{3+} concentration (mol/l) to the sum of concentration (mol/l) of Fe^{2+} and Fe^{3+} in the electrolytic solution is limited within a high range of from 0.5 to under 1.0 for the following reason.

Oxygen in the Fe-Ni-O film is considered to mainly comprise oxygen existent in eutectic iron oxide. In order for the content of this oxygen in the film to be at least a prescribed value, it is advantageous to increase the concentration ratio of Fe^{3+} precipitated with a low pH over that of Fe^{2+} relative to the concentration ratio of Fe^{2+} . To achieve an oxygen content in the Fe-Ni-O film of at least 0.5 wt.%, the ratio of concentration (mol/l) of Fe^{3+} to the sum of concentration (mol/l) of Fe^{2+} and Fe^{3+} must be at least 0.5. A higher ratio (mol/l) of the Fe^{3+} concentration brings about a higher efficiency of achieving eutectic iron oxides in the Fe-Ni-O film. Fe^{3+} produces hydroxides at a lower pH than that of Fe^{2+} (for example, a concentration of 0.1 mol/l corresponds to a pH of 2.2 and 7.5, respectively), and this facilitates eutectic precipitation of oxides as a result of increase in pH on the surface due to electrolysis.

It is not necessary to limit the electrolytic bath temperature within a particular range. With a temperature of under 30 °C, however, conductivity of the electrolytic bath becomes lower, leading to a higher electrolytic voltage. With a temperature of over 70 °C, on the other hand, there is an increase in the amount of vapor of the electrolytic solution, thus making it difficult to control ion concentration of nickel and iron ions. It should therefore preferably be within a range of from 30 to 70 °C.

There is no particular restrictions on current density of electrolytic plating. With a current density of under 1 A/dm², however, there occurs a considerable decrease in current efficiency because hydrogenation takes a main part in the cathodic reactions. With a current density of over 150 A/dm², on the other hand, burnt deposits proceeds, entrapping much hydroxides of nickel and iron, leading to a lower weldability. Current density should therefore be limited within a range of from 1 to 150 A/dm².

In the zinciferous plated steel sheet used for forming the Fe-Ni-O film on the surface thereof in the present invention, the surface of the plating layer should preferably comprise an alloyed dip-plating layer having an iron content of from 7 to 15 wt.%, an electroplating layer, or a dip-plating layer. The reason is that, because a zinciferous plated steel sheet having any of these plating layers is inferior to a cold-rolled steel sheet or a zinc-nickel alloy plated steel sheet in workability, or particularly, press formability, and spot weldability, formation of the Fe-Ni-O film of the present invention on the foregoing plating layer provides a remarkable improvement effect of press formability and spot weldability.

The electrolytic solution may contain cations such metals as Zn, Co, Mn, Mo, Al, Ti, Sn, W, Si, Pb, Nb and Ta, which are contained in the zinciferous plating layer, oxides and hydroxides of these metals, and anions other than chlorine cation.

The zinciferous plated steel sheet used in the present invention is a steel sheet on the surface of which a zinciferous plating layer is formed by any of the dip plating method, the electroplating method and the vapor plating method. The zinciferous plating layer comprises, in addition to pure zinc, a single-layer or a plurality of plating layers containing one or more of such metals as Fe, Ni, Co, Mn, Cr, Al, Mo, Ti, Si, W, Sn, Pb, Nb and Ta (Si is also regarded as a metal), or oxides thereof, or organic substances. The layer may contain furthermore such fine particles as SiO_2 and Al_2O_3 . The zinciferous plating layer may comprise a plurality of layers, each containing the same ingredients with different contents. Furthermore, the zinciferous plating layer may comprise a plurality of layers, each containing the same ingredients of which the contents sequentially vary in the thickness direction, known as "functional gradient plating layers".

The Fe-Ni-O film formed on the surface of the plating layer of the zinciferous plated steel sheet under the foregoing limiting conditions eliminates sticking between the steel sheet and the die during press forming, reduces sliding resistance, improves flowing-in into the die, inhibits formation of a brittle alloy layer between the sheet and the copper electrode during spot welding, thus improving continuous spot weldability and improves adhesiveness under the effect of the film containing Fe oxides. With a coating weight of the Fe-Ni-O film (total conversion weight of metal elements in the film) of under 10 mg/m², the effect of improving press formability is unavailable. With a coating weight of over 1,500 mg/m², on the other hand, the improving effect of press formability is saturated. The coating weight (total conversion weight of metal elements in the film) of the Fe-Ni-O film should therefore preferably be within a range of from 10 to 1,500 mg/m².

The improving effect of adhesiveness cannot be achieved if the ratio of Fe content (wt.%) to the sum of Fe content and Ni content (wt.%) in the Fe-Ni-O film ($\text{Fe}/(\text{Fe} + \text{Ni})$ in the film) is under 0.05. When $\text{Fe}/(\text{Fe} + \text{Ni})$ in the film is over 0.9, on the other hand, the Ni content in the film decreases, resulting in a decreased ratio of Zn-Ni alloy of a high melting point formed during welding, and this results in more serious deterioration of the electrode, thus preventing achievement of the improving effect of spot weldability.

The ratio $\text{Fe}/(\text{Fe} + \text{Ni})$ in the film should therefore preferably be within a range of from 0.05 to 0.9, or more preferably, from 0.1 to 0.5.

The preferable range of the oxygen content in the Fe-Ni-O film is from 0.5 to 10 wt.%. With an oxygen content of under 0.5 wt.%, metal properties of the film becomes more apparent, reducing the improving effect of press formability. With an oxygen content of over 10 wt.%, on the other hand, the amount of oxides becomes too large, resulting in an increase in electric resistance of the surface, a decrease in weldability, and inhibited production of phosphate crystals, leading to deterioration of chemical treatability.

Examples

The zinciferous plated steel sheet before application of electrolysis by the method of the present invention or a comparative method is any of the following plating types GA, GI and EG formed thereon:

GA: There is formed an alloyed dip-plating layer comprising 10 wt.% Fe and the balance Zn in a coating weight of 60 g/m² for each of the both surfaces;

GI: There is formed a dip-plating layer in a coating weight of 90 g/m² for each of the both surfaces;

EG: There is formed an electroplating layer in a coating weight of 40 g/m² for each of the both surfaces.

With the zinciferous plated steel sheet as the cathode, an electrolytic treatment was applied in a mixed solution containing nickel sulfate, ferrous sulfate and ferric sulfate in prescribed concentrations, thereby forming an Fe-Ni-O film on the surface of the zinciferous plated steel sheet to prepare a sample. For some samples, electrolytic treatment was omitted.

Table 1 shows electrolytic conditions for Examples 1 to 20 subjected to electrolysis under conditions within the scope of the present invention, and Comparative Examples 2, 3 and 5 subjected to electrolysis under conditions, at least one of which was outside the scope of the present invention. For the Comparative Examples 1, 4 and 6 in Table 1, treatment was limited to dip into electrolytic solution without applying an electrolytic treatment. Table 1 shows also plating types of steel sheets before application of electrolytic treatment, chemical composition of electrolytic solution, pH, temperature, current density and time.

Table 1

Test Division	Type of Plating	Electrolytic Condition for Film Forming						Current Density (A/cm ²)	Turn-on Period (sec)
		Chemical Composition of Electrolyte		pH	Temperature (°C)	Electrolyte			
		Nickel Sulfate Content and Total (Ferrous Sulfate) + (Ferric Sulfate) Content	Fe ³⁺ / (Fe ²⁺ +Fe ³⁺)						
Comparative Example 1	GA	Nickel Sulfate: 1.0 mol/l Ferrous Sulfate + Ferric Sulfate: 0.2 mol/l	-	2	50	-	-	-	-
Comparative Example 2	GA		0.4	2	50	5	5	-	-
Example 1	GA		0.5	2	50	5	5	1	1
Example 2	GA		0.6	2	50	5	5	1	1
Example 3	GA		0.7	2	50	5	5	1	1
Example 4	GA		0.8	2	50	5	5	1	1
Example 5	GA		0.9	2	50	5	5	1	1
Example 6	GA		0.99	2	50	5	5	1	1
Comparative Example 3	GA	Nickel Sulfate: 0.5 mol/l Ferrous Sulfate + Ferric Sulfate: 0.2 mol/l	0.4	1.5	50	10	10	1	1
Example 7	GA		0.5	1.5	50	10	10	1	1
Example 8	GA		0.6	1.5	50	10	10	1	1
Example 9	GA		0.7	1.5	50	10	10	1	1
Example 10	GA		0.8	1.5	50	10	10	1	1
Example 11	GA		0.9	1.5	50	10	10	1	1
Example 12	GA		0.99	1.5	50	10	10	1	1
Comparative Example 4	EG	Nickel Sulfate: 1.5 mol/l Ferrous Sulfate + Ferric Sulfate: 0.4 mol/l	-	1.2	60	-	-	-	-
Comparative Example 5	EG		0.4	1.2	60	20	20	1	1
Example 13	EG		0.5	1.2	60	20	20	1	1
Example 14	EG		0.6	1.2	60	20	20	1	1
Example 15	EG		0.7	1.2	60	20	20	1	1
Example 16	EG		0.8	1.2	60	20	20	1	1
Example 17	EG		0.9	1.2	60	20	20	1	1
Example 18	EG		0.99	1.2	60	20	20	1	1
Comparative Example 6	GI	Nickel Sulfate: 1.5 mol/l Ferrous Sulfate + Ferric Sulfate: 0.4 mol/l	-	2	50	-	-	-	-
Comparative Example 7	GI		0.4	2	50	5	5	1	1
Example 19	GI		0.5	2	50	5	5	1	1
Example 20	GI		0.9	2	50	5	5	1	1

The ratio of concentration of ferrous sulfate to ferric sulfate in the electrolytic solution was controlled by adjusting the concentration of chemicals added. When the ratio of ferrous sulfate to ferric sulfate varied according as electrolysis proceeds, however, the ratio was controlled by adding an oxidizing agent such as hydrogen peroxide into the electrolytic solution to oxidize ferrous ion into ferric ion, or by bringing ferric ion into contact with metallic iron to reduce it into ferrous ion.

For the Fe-Ni-O film formed on each sample treated by electrolysis as described above, the coating weight of the film (total conversion weight of metal elements in the film), the ratio of Fe content (wt.%) to the sum of Fe and Ni contents (wt.%) in the film, and oxygen content in the film were measured as follows.

5 [Measurement of coating weight of film (total conversion weight of metal elements in film) and Fe/(Fe + Ni) in film]

For the samples of plating types GI and EG, the coating weight of the Fe-Ni-O film (total conversion weight of metal elements in the film) and chemical composition were measured by dissolving the Fe-Ni-O film, together with the plating layer thereunder (zinciferous plating layer; the same applies also hereafter), with diluted hydrochloric acid to cause
10 peeling, and performing quantitative analysis of Fe and Ni by the ICP method (abbreviation of Inductively Coupled Plasma Spectroscopic method). Then, the ratio Fe/(Fe + Ni) in the film was calculated.

For the samples of plating types GA, it was difficult to completely separate the component elements in the upper Fe-Ni-O film from those of the lower plating layer by the ICP method, since the lower plating layer contained the component elements of the Fe-Ni-O film. Therefore, only component elements of the Fe-Ni-O film not contained in the lower
15 plating layer were quantitatively analyzed by the ICP method. Further, after Ar ion sputtering, the chemical composition distribution of the individual component elements in the Fe-Ni-O film in terms of the depth of the plating layer was measured by repeating measurement of the individual component elements of the Fe-Ni-O film by the XPS method(abbreviation of X-ray Photoelectron Spectroscopic method), starting from the film surface. In this measurement, the distance
20 between the depth at which a component element of the Fe-Ni-O film not contained in the lower plating layer showed a maximum concentration and the position equal to a half the depth at which that element was no more detected was taken as the thickness of the Fe-Ni-O film. The coating weight of the Fe-Ni-O film (total conversion weight of metal elements in the film) and the chemical composition were calculated from the results of the ICP method and those of the XPS method. Then, the ratio Fe/(Fe + Ni) was calculated.

25 [Measurement of oxygen content in film]

The oxygen content in the film was determined from the result of analysis in the depth direction based on the Auger electron spectroscopy (AES).

Table 2 shows the results of measurement of the coating weight of the Fe-Ni-O film (total conversion weight of metal
30 elements in the film), the ratio Fe/(Fe + Ni) in the film, and oxygen content in the film for the individual samples obtained from Examples 1 to 20 and Comparative Examples 1 to 7, i.e., samples Nos. 1 to 20 of the present invention and comparative samples Nos. 1 to 7.

Table 2

Test Division	Sample	Fe-Ni-O Film				Properties			
		Coating Weight (mg/m ²) (Total Conversion Weight of Metal Elements in Film)	Fe Ratio (Fe/Fe+Ni) (-)	Oxygen Content (wt. %)	Press Formability		Spot Weldability	Adhesiveness	
					Frictional Coefficient (-)				
					Bead Type: A	Bead Type: B			
Comparative Example 1	Comparative Sample 1	0	-	-	0.171	0.255	2900	6.8	
Comparative Example 2	Comparative Sample 2	75	0.26	0.40	0.147	0.173	5200	9.5	
Example 1	Sample of Invention 1	74	0.25	0.50	0.125	0.151	5100	12.0	
Example 2	Sample of Invention 2	72	0.25	1.00	0.127	0.150	5100	12.1	
Example 3	Sample of Invention 3	70	0.26	4.00	0.125	0.151	5200	12.4	
Example 4	Sample of Invention 4	64	0.24	6.00	0.124	0.152	5400	12.3	
Example 5	Sample of Invention 5	66	0.27	7.00	0.125	0.147	5200	12.5	
Example 6	Sample of Invention 6	62	0.26	8.00	0.123	0.148	5100	12.4	
Comparative Example 3	Comparative Sample 3	80	0.42	0.30	0.146	0.168	5000	8.6	
Example 7	Sample of Invention 7	78	0.40	0.60	0.123	0.148	5100	12.2	
Example 8	Sample of Invention 8	75	0.42	1.90	0.124	0.142	5000	12.1	
Example 9	Sample of Invention 9	82	0.41	4.00	0.125	0.144	5200	12.2	
Example 10	Sample of Invention 10	80	0.40	5.00	0.125	0.143	5200	12.1	
Example 11	Sample of Invention 11	82	0.44	7.00	0.125	0.142	5200	12.6	
Example 12	Sample of Invention 12	83	0.40	9.00	0.126	0.144	5000	12.9	
Comparative Example 4	Comparative Sample 4	0	-	-	0.224	0.306	1900	5.6	
Comparative Example 5	Comparative Sample 5	100	0.61	0.30	0.146	0.168	3900	7.6	
Example 13	Sample of Invention 13	105	0.60	0.60	0.126	0.146	4100	12.6	
Example 14	Sample of Invention 14	105	0.62	1.50	0.124	0.146	4100	12.4	
Example 15	Sample of Invention 15	110	0.62	3.60	0.124	0.145	4100	12.4	
Example 16	Sample of Invention 16	102	0.62	4.20	0.123	0.144	4100	12.3	
Example 17	Sample of Invention 17	100	0.60	6.60	0.125	0.148	4100	12.0	
Example 18	Sample of Invention 18	100	0.61	8.50	0.124	0.145	4100	12.3	
Comparative Example 6	Comparative Sample 6	0	-	-	0.210	0.320	900	3.8	
Comparative Example 7	Comparative Sample 7	70	0.25	0.40	0.151	0.175	3800	8.0	
Example 19	Sample of Invention 19	72	0.25	0.55	0.121	0.149	3900	12.1	
Example 20	Sample of Invention 20	72	0.24	7.00	0.123	0.152	4000	12.1	

Subsequently, measurement of frictional coefficient, a continuous spot weldability test and an adhesiveness test in spot welding were carried out in the manner as described below with a view to evaluating press formability, spot weldability and adhesiveness for samples of the invention Nos. 1 to 20 and comparative samples Nos. 1 to 7.

[Measurement of frictional coefficient]

Fig. 1 is a schematic front view illustrating the measuring apparatus of frictional coefficient. As shown in Fig. 1, a frictional coefficient measuring sample 1 taken from a sample was fixed on a sample stand 2 which was fixed on the upper surface of a horizontally movable sliding table 3. The lower surface of the sliding table 3 was provided with a vertically movable sliding table support 5 having rollers 4 in contact with the lower surface. A first load cell 7 for measuring a pressing load N onto a frictional coefficient measuring sample 1 by a bead 6 by pushing up the sliding table support 5 was attached to the sliding table support 5. Under the action of this pressing force, an end in the horizontally moving direction of the sliding table 3 is attached with a second load cell 8 for measuring sliding resistance F for horizontally moving the sliding table 3.

The frictional coefficient μ between the sample and the bead was calculated by a formula: $\mu = F/N$. In this calculation, the pressing load was 400 kgf and a pulling speed of sample (horizontal moving speed of the sliding table 3) was 100 cm/minute. Beads of the following two kinds of size and shape were employed:

Fig. 2 is a schematic perspective view illustrating the shape and size of a bead of a first type (hereinafter referred to as the "bead type A"). Sliding is conducted in a state in which the lower surface of the bead 6 is pressed against the surface of the sample 1. The lower surface thereof has a plane with a width of 10 mm and a length of 3 mm in the sliding direction, and a 1/4 cylinder surface having a radius of curvature of 4.5 mm is in contact with each of lines of a width of 10 mm on the front and back surfaces as shown in Fig. 2.

Fig. 3 is a schematic perspective view illustrating the shape and size of a bead of a second type (hereinafter referred to as the "bead type B"). In the bead type B, the length in the sliding direction of the sliding surface, which is 3 mm in the bead type A, is increased to 60 mm, and the other portions are the same as those in the bead type A.

In the both types A and B, NOX RUST 550 HN made by Nihon Perkerizing Co. Ltd. was applied as a lubricant oil onto the upper surface of the sample 1 for the measurement of frictional coefficient, and a test was carried out.

[Continuous spot weldability test]

Two samples of the same No. were placed one on top of the other between a pair of electrode chips of a spot welding machine, and electrifying the piled samples while applying a pressure to same, thereby continuously carrying out a resistance-welding with a concentrated welding current, i.e., a spot-welding, under the following conditions:

- * Electrode chip: A dome type chip having an end diameter of 6 mm
- * Pressing force: 250 kgf
- * Welding time: 12 cycles (60 Hz)
- * Welding current: 11.0 KA
- * Welding speed: 1 spot/sec

Continuous spot weldability was evaluated in terms of the number of continuous spot-welding runs performed before the diameter of a metallic portion having melted and solidified (hereinafter referred to as a "nugget") produced in a weld zone between the two piled samples during spot-welding becomes under $4 \times t^{1/2}$ (t: thickness of a sample). This number of spots is hereinafter referred to as the "electrode life."

[Adhesiveness test]

The following adhesiveness test piece was prepared from each of the samples.

Fig. 4 is a schematic perspective view illustrating the assembly process. As shown in Fig. 4, a test piece 13 was prepared by placing two samples 10 having a width of 25 mm and a length of 200 mm one on top of the other via a spacer 11 having a diameter of 0.15 mm in between so that the adhesive agent 12 had a thickness of 0.15 mm, and bonding these two samples. The thus prepared test piece was subjected to a baking treatment at 150 °C for ten minutes.

The thus prepared test piece was folded into a T shape as shown in Fig. 5, subjected to a tensile test at a speed of 200 mm/min by means of a tensile tester, and an average peeloff strength ($n = 3$) was measured upon peeling of the test piece. Peeloff strength was calculated by determining an average load from a load chart of tensile load curve obtained upon peeling and the result was expressed in kgf/25 mm. In Fig. 5, P represents tensile load. As the adhesive agent, there was used a vinyl chloride resin type adhesive agent for hemflange adhesion.

Table 2 shows the results of determination of frictional coefficient, continuous spot welding runs and peeloff strength of the individual samples obtained in the foregoing tests. From Table 2, the following points are evident.

All the samples of the invention Nos. 1 to 20 show a small frictional coefficient and a satisfactory press formability. In terms of the continuous spot welding runs, any of the samples of the invention Nos. 1 to 20 is larger in this number by at least 1,000 points than the comparative samples 1, 4 and 6 not subjected to electrolysis, leading to a longer elec-

trode life. Any of the samples of the invention shows a peeloff strength of at least 12 kgf/25 mm, corresponding to a very good adhesiveness.

For all the comparative samples Nos. 1 to 7 outside the scope of the present invention, at least one of frictional coefficient, the continuous spot welding runs and peeloff strength is defective and is low in at least any of press formability, spot weldability and adhesiveness.

According to the present invention having the construction as described above, the Fe-Ni-O film formed on the surface of the plating layer of the zinciferous plated steel sheet has a higher hardness and a higher melting point than a zinc or zinc alloy plating layer. Presence of this film in an appropriate amount reduces sliding resistance between the surface of the plating layer and a press die during press forming of the zinciferous plated steel sheet, and enables the zinciferous plated steel sheet to easily flow into the die. The Fe-Ni-O film of a high melting point permits improvement of continuous spot weldability. Presence of Fe oxides in the Fe-Ni-O film improves peeloff strength of bonded substrates. Furthermore, as it is possible to adjust the oxygen content in the film to prevent it from exceeding a certain limit, a zinciferous plated steel sheet excellent in chemical treatability is available. According to the present invention, therefore, there is provided a zinciferous plated steel sheet excellent in press formability, spot weldability and adhesiveness, thus providing industrially very useful effects.

EMBODIMENT 2

The Inventors earnestly conducted research for solving the above-described problems. As a result, the Inventors have found that the press-formability, spot-weldability, and adhesiveness of a zinciferous plated steel sheet can be markedly improved by forming a proper Fe-Ni-O film on its surface.

According to the Inventor's findings, the proper Fe-Ni-O film satisfies the following requirements.

- (1) The coating weight is within a range of 10 through 1500 mg/m² in terms of total weight of the metals in the film.
- (2) The ratio of the Fe content (% by weight) against the sum of the Fe content and Ni content (% by weight) in the film is within a range of 0.05 through 0.9, and preferably, within a range of 0.1 through 0.5. [Hereinafter, this ratio may be referred to as Fe ratio in a film, and expressed by $\text{Fe}/(\text{Fe}+\text{Ni})$.]
- (3) The oxygen content in the film is within a range of 0.5 through 10% by weight.

The cause of inferiority of zinciferous plated steel sheets to cold-rolled steel sheets in press-formability is the increased sliding resistance attributed to sticking between the die and zinc having a low melting point which occurs under a high surface pressure. What is effective to avoid this is to form, on the surface of a zinciferous plated steel sheet, a film which is harder than zinc or zinc-alloy plating layer and has a higher melting point. This decreases the sliding resistance between the surface of the plating layer and the press die during press forming, allows the zinciferous plated steel sheet to easily flow into the press mold, and therefore, improves press-formability.

Meanwhile, the cause of the inferiority of zinciferous plated steel sheets to cold-rolled steel sheets in continuous spot-weldability during spot welding is the rapid electrode deterioration attributed to a brittle alloy layer which is formed on the electrode by the contact of melted zinc with electrode copper during welding. Here, it has been recognized as effective for improving the continuous spot-weldability of zinciferous plated steel sheets to form a film having a high melting point on their surfaces. The Inventors conducted research on various coats in order to improve the spot-weldability of zinciferous plated steel sheets, and as a result, they have found that a Ni metal is especially effective. Though the mechanism of this effectiveness has not yet been clarified in detail, it may be attributed to the high melting point and the high electric conductivity of the Ni metal.

Though the fact that zinciferous plated steel sheets are inferior to cold-rolled steel sheets in adhesiveness properties is already known, the reason for this has not been revealed yet. Under the circumstances, the Inventors conducted research on the reason. As a result, adhesiveness have been found to be controlled by the composition of the oxide film on the surface of the steel sheet. In cold-rolled steel sheets, the oxide film on the surface of the steel sheet principally consist of Fe oxides. In contrast, the principal ingredient in a zinciferous plated steel sheet is Zn oxide. Differences in adhesiveness depend on the composition of the oxide film, and the Zn oxide is inferior to the Fe oxide in adhesiveness. Consequently, improvement in the adhesiveness of zinciferous plated steel sheet has been accomplished by forming a film containing an Fe oxide on their surface in the manner of the present invention.

As described above, the oxygen content in the Fe-Ni-O film should essentially be within a range of 0.5 through 10 wt.%. The Inventors have also obtained the following findings to achieve the above essential requirement.

The Fe-Ni-O film contains oxygen principally in the iron oxide formed as eutectoid. For achieving such an eutectic iron oxide by cathode electrolysis, the deposition rate of the Fe-Ni-O film should be accelerated so that the diffusion rate of the metal ions cannot catch up with it, namely, a state of so-called burnt deposit should be generated. Specifically, the electrolysis should be performed essentially with a current density beyond the limiting current which is determined according to the composition of the electrolytic plating bath and the electrolysis conditions.

The present invention has been accomplished based on the above findings, provides a method for a zinciferous

plated steel sheet excellent in press-formability, spot-weldability, and adhesiveness by properly forming an Fe-Ni-O film on the surface of the plating layer on a zinciferous plated steel sheet, and is illustrated below.

Here, as to the micro-texture and formation of the Fe-Ni-O film, the bonding conditions of elements constituting the film are not limited, as far as the film comprises a mixture containing at least metals of Ni and Fe, and oxides of Ni and Fe.

The method for manufacturing a zinciferous steel sheet according to Embodiment 2 comprises forming a film on the surface of the plating layer on a zinciferous plated steel sheet by electrolysis using the zinciferous plated steel sheet as a cathode in a plating solution which comprises an aqueous solution containing nickel sulfate and ferrous sulfate, wherein the electrolysis is performed under the following conditions to form an Fe-Ni-O film: Total concentration of nickel sulfate and ferrous sulfate in the plating solution is within a range of 0.1 through 2.0 mol/l, and preferably, within a range of 0.1 through 0.5 mol/l; the pH of the solution is within a range of 1.0 through 3.0; and the relationship between the sum of the concentrations of the nickel ions and ferrous ions in the plating solution, M (mol/l), the mean flow rate of the plating solution, U (m/s), and the current density in the electrolysis, I_K (A/dm²) satisfies the following equation (1).

$$I_K / (U^{1/2} M) = 50 \text{ through } 150 \quad (1)$$

The plating layer on the surface of the steel sheet can be an alloyed zinc dip-plating layer containing iron in an amount within a range of 7 through 15 wt.%. Furthermore, the plating layer on the surface of the steel sheet can be a zinc electroplating layer or a zinc dip-plating layer.

Incidentally, in the present patent specification, the Fe-Ni-O film formed as an upper layer on the surface of the zinciferous plating layer is referred to as "film" distinguishingly from the zinc or zinciferous plating layer as a lower layer which is referred to as "plating layer".

Next, the reasons for the above-described limitation in the manufacturing conditions of the present invention will be illustrated.

In the present invention, nickel sulfate and ferrous sulfate are used as the ingredients of the plating solution used for formation of the Fe-Ni-O film on the surface of the plating layer on a zinciferous plated steel sheet since these sulfates are suitable for efficient introduction of Fe, Ni, and O into the film to be formed when the zinciferous plated steel sheet to be provided with the Fe-Ni-O film is allowed to be a cathode.

The following are basis for specifying the total concentration of nickel sulfate and ferrous sulfate to be 0.1 through 2.0 mol/l, and preferably, 0.1 through 0.5 mol/l.

With a total concentration below 0.1 mol/l, the voltage for electrolysis will be higher due to the lower conductivity of the plating bath, and therefore, a rectifier applicable to a higher voltage is required. For this reason, such a low concentration is unsuitable.

On the other hand, with a total concentration exceeding 2.0 mol/l, nickel sulfate and/or ferrous sulfate will precipitate at a lower temperature since the concentration will reach the upper limit of the solubility of nickel sulfate and/or ferrous sulfate. Further, the limiting current density will be large, and thereby, the state of burnt deposits cannot be achieved unless the electrolysis is carried out with a markedly higher current density. Moreover, in such a case, the electrolyzing time to obtain the optimum coating weight of the Fe-Ni-O film will be as remarkably short as below 1 second, and such electrolysis will be difficult to control. From these view points, the total concentration should be set below 2.0 mol/l, and preferably, 0.5 mol/l or less.

Additionally, the electrolytic solution may contain cations, hydroxides, and/or oxides such as of Zn, Co, Mn, Mo, Al, Ti, Sn, W, Si, Pb, Nb, and Ta, which may be contained in the plating layer on the zinciferous plated steel sheet to be used in the present invention, and also, the solution may contain anions which do not affect the electrolytic reaction and are not chloride ions, fluoride ions, bromide ions, nor iodide ions.

The following are the reasons for the use of the electrolytic solution which has a pH value within a range of 1.0 through 3.0.

With a pH value of the electrolytic solution below 1.0, hydrogen gas will be a principal resultant of the electrolytic reaction at the cathode while severely decreasing the current efficiency. On the other hand, with a pH value of the electrolytic solution exceeding 3, ferric hydroxide will precipitate.

The temperature of the plating bath may not necessarily be limited. However, with a temperature below 30 °C, the conductivity of the plating bath will be lower, and thereby, the voltage for the electrolysis will be higher. In such a case, the oxygen content in the Fe-Ni-O film tends to be larger. On the other hand, the control of the concentration of nickel ions and ferrous ions will be difficult with a temperature exceeding 70 °C since the vaporizing amount of the electrolytic solution will be large. Consequently, the temperature of the plating bath should preferably be 30 through 70 °C.

In general, the limiting current density I_{Kd} , which is a limitation for non-occurrence of burnt deposits and which relates to ingredient metals, is expressed by the following equation (2), and is proportional to the diffusion coefficient D and the ionic concentration M of the metal to be deposited but is inversely proportional to the thickness δ of the diffusion layer to be formed on the surface of the steel sheets.

$$I_{kd} = nFD(M/\delta) \quad (2)$$

In the above equation, n is the number of the valency of the metal ion; F is the Faraday constant; D is the diffusion coefficient of the metal ion; and M is the ionic concentration of the metal to be deposited.

In contrast, the Inventors conducted a study on the relationship between the limiting current density I_{kd} , the ionic concentration M of the metal to be deposited, the mean flow rate U of the plating solution, and the temperature of the plating bath. As a result, the limiting current density I_{kd} has been found to be proportional to the ionic concentration M of the metal to be deposited and to the square root of the mean flow rate U of the plating solution. Specifically, the relationship expressed by the following equation (3) has been found.

$$I_{kd} = k(U^{1/2}M) \quad (3)$$

I_{kd} : limiting current density (A/dm^2)

U : mean flow rate of the plating solution (m/s)

M : sum of the ionic concentrations of all metals in the plating solution (mol/l)

k : constant

The following equation (4) is obtained by modifying the equation (3).

$$I_{kd} / (U^{1/2} M) = k \quad (4)$$

As a result of further research, the Inventors have found that the constant k should be 50 or more to achieve 0.5 wt.% or more of the oxygen content in the Fe-Ni-O film, and that the constant k should be 150 or less to achieve 10 wt.% or less of the oxygen content.

Accordingly, to restrict the oxygen content in the Fe-Ni-O film within a range of 0.5 through 10 wt.%, the sum of ionic concentrations of all metals in the plating solution, M (mol/l), the mean flow rate of the plating solution, U (m/s), and the current density in the electrolysis, I_K (A/dm^2) should satisfy the relationship expressed by the following equation (1).

$$I_K / (U^{1/2} M) = 50 \text{ through } 150 \quad (1)$$

Here, the mean flow rate of the plating solution indicates the mean value of the flow rate at the middle point between the anode and the cathode.

Incidentally, in the present invention, a large part of the metal ions in the plating bath for deposition are nickel ions and ferrous ions, and other ions do not essentially affect the deposition of the Fe-Ni-O film except for ferric ions. The concentration of ferric ion should be limited to 0.09 mol/l or less since ferric ion decreases the deposition efficiency of the Fe-Ni-O film and causes deterioration of the zinciferous plated steel sheet.

As to the zinciferous plated steel sheet to be provided with an Fe-Ni-O film on the surface in the present invention, the plating layer on the surface should preferably comprise an alloyed zinc dip-plating layer containing 7 through 15 wt.% iron, zinc electroplating layer, or zinc dip-plating layer. The zinciferous plated steel sheets having such plating layer are inferior to cold-rolled steel sheets and zinc-nickel-alloy-plated steel sheets in processability, especially press-formability, and weldability or the like. Such a zinciferous plated steel sheet will, therefore, be considerably improved in press-formability and spot-weldability by forming the Fe-Ni-O film on the surface of the above-mentioned plating layer.

Incidentally, the zinciferous plated steel sheet to be used in the present invention is, in the state previous to formation of the Fe-Ni-O film, a steel sheet provided with a zinc plating layer on its surface by dip-plating, electroplating, vapor deposition, or the like. The ingredients of the zinc plating layer are, in addition to pure zinc, metals such as Fe, Ni, Co, Mn, Cr, Al, Mo, Ti, Si, W, Sn, Pb, and Ta (wherein Si is also regarded as a metal), or oxide thereof, or the plating layer may comprise a single or a plurality of layers containing one or more organic substances. Additionally, the above-mentioned plating layer may contain fine particles such as SiO_2 particles and Al_2O_3 particles. The zinciferous plating layer may comprise a plurality of layers, each containing the same ingredients with different contents. Furthermore, the zinciferous plating layer may comprise a plurality of layers, each containing the same ingredients of which the contents sequentially vary in the thickness direction, known as "functional gradient plating layers".

When an Fe-Ni-O film is formed on the surface of the plating layer on a zinciferous plated steel sheet according to the specified conditions as described above, the following advantages or effects can be achieved: The sliding resistance will decrease since sticking between the steel sheet and the die will not occur during press forming, and therefore, the steel sheet will readily flow into the mold; on spot-welding, the continuous spot-weldability will be improved since the formation of a brittle alloy layer between the steel sheet and the electrode copper can be inhibited; and adhesiveness will be improved by the function of the film containing an Fe oxide.

The Fe-Ni-O film formed on the surface of the plating layer of a zinciferous plated steel sheet according to the specified conditions as described above brings about the following advantages and effects: Sticking between the steel sheet

and the die during press forming does not occur, and therefore, sliding resistance decreases and the steel sheet readily flows into the mold; during spot-welding, the formation of the brittle alloy layer between the electrode copper and the steel is inhibited to improve continuous spot-weldability; and adhesiveness are improved by the function of the film containing an Fe oxide. However, when the coating weight of the Fe-Ni-O film is below 10 mg/m², press-formability cannot be improved. On the other hand, with the coating weight exceeding 1500 mg/m², the improving effect in press-formability will be saturated. Accordingly, the coating weight of the Fe-Ni-O film should preferably be within a range of 10 through 1500 mg/m².

The improving effect in adhesiveness cannot be exhibited when the ratio of the Fe content (% by weight) to the sum of the Fe content and the Ni content (% by weight) in the Fe-Ni-O film, namely, the Fe/(Fe+Ni) in the film, is below 0.05. On the other hand, when the Fe/(Fe+Ni) in the film exceeds 0.9, the ratio of the Zn-Ni alloy which is formed during welding and which has a higher melting point will decrease since the content of Ni present in the film will decrease. As a result, the electrodes will rapidly deteriorate, and the improving effect in spot-weldability cannot be exhibited.

Consequently, the Fe/(Fe+Ni) in the film should be within a range of 0.05 through 0.9, and preferably, 0.1 through 0.5.

The oxygen content in the Fe-Ni-O film should preferably be within a range of 0.5 through 10 wt.%. With the oxygen content below 0.5 wt.%, the metal properties of the film will be predominant, and therefore, the effect of improving press-formability will be small. On the other hand, with the oxygen content exceeding 10 wt.%, the amounts of the oxides to be formed will be too much. As a result, electrical resistance will increase and weldability will deteriorate. Further, chemical treatability will deteriorate since the formation of phosphate crystals will be inhibited.

Examples

The zinciferous plated steel sheets each of which is provided with a plating layer of the GA, GI, or EG type below were used as the zinciferous plated steel sheets to be subjected to the electrolytic treatment according to methods of the present invention or comparative methods.

GA: alloyed zinc dip-plating layer comprising 10 wt.% Fe and the balance Zn is formed on both surfaces with a coating weight for each surface of 60 g/m².

GI: zinc dip-plating layer is formed on both surfaces with a coating weight for each surface of 90 g/m².

EG: electroplating layer is formed on both surfaces with a coating weight for each surface of 40 g/m².

Each zinciferous plated steel sheet as described above was set as a cathode, and an electrolytic treatment was performed in a mixture of a nickel sulfate solution and a ferrous sulfate solution having predetermined concentrations to form an Fe-Ni-O film on the surface of the zinciferous plated steel sheet. Here, some of the zinciferous plated steel sheets were merely dipped in the electrolytic solution without being subjected to the electrolytic treatment.

Tables 3 and 4 show the conditions for the electrolytic treatments in Example 1 through 30, which were subjected to the electrolytic treatments with the conditions in the scope of the present invention; those in Comparative Examples 2 through 12, 14, 15, 17, and 18, in each of which, at least one condition for the electrolytic treatment was out of the scope of the present invention; and the dipping conditions in Comparative Examples 1, 13, and 16, which were not subjected to electrolytic treatments. The tables also show the types of the plating layers on the steel sheets to be subjected to the electrolytic treatments; the ingredient contents, the pH values, and the temperatures of the electrolytic solutions; and the plating conditions.

As is obvious from Tables 3 and 4, the ingredient contents and the pH values of the electrolytic solutions were within the scope of the present invention both in the examples and the comparative examples. In all of the comparative examples, however, one requirement of the present invention, namely, the following equation (1), was not satisfied.

$$I_K/(U^{1/2}M) = 50 \text{ through } 150$$

Table 3

No	Test Sample	Type of plating	Ingredients, Contents, pH and Temperature of Electrolytic Solution	Plating Conditions			
				Current Density : I_k (A/dm ²)	Flow Rate of Plating Solution: U (m/S)	$\frac{I_k}{U^{1/2}}$	Plating Time (s)
1	Comparative Example 1	GA	Nickel Sulfate:	-	-	-	-
2	Comparative Example 2	GA	0.08 mol/l	4	1	40	1
3	Example 1	GA	Ferrous Sulfate	5	1	50	1
4	Example 2	GA	0.02 mol/l	8	1	80	1
5	Example 3	GA	pH: 2	10	1	100	1
6	Example 4	GA	Temperature:	12	1	120	1
7	Example 5	GA	50 °C	15	1	150	1
8	Comparative Example 3	GA		17	1	170	1
9	Comparative Example 4	GA	Nickel Sulfate:	8	1	40	1
10	Example 6	GA	0.16 mol/l	10	1	50	1
11	Example 7	GA	Ferrous Sulfate	16	1	80	1
12	Example 8	GA	0.04 mol/l	20	1	100	1
13	Example 9	GA	pH: 2	24	1	120	1
14	Example 10	GA	Temperature:	30	1	150	1
15	Comparative Example 5	GA	50 °C	34	1	170	1
16	Comparative Example 6	GA	Nickel Sulfate:	20	1	40	1
17	Example 11	GA	0.4 mol/l	25	1	50	1
18	Example 12	GA	Ferrous Sulfate	40	1	80	1
19	Example 13	GA	0.1 mol/l	50	1	100	1
20	Example 14	GA	pH: 2	60	1	120	1
21	Example 15	GA	Temperature:	75	1	150	1
22	Comparative Example 7	GA	50 °C	85	1	170	1

Note M: The sum of Ni ion concentration and ferrous ion concentration (mol/l)

Table 4

No	Test Sample	Type of Plating	Ingredients, Contents, pH and Temperature of Electrolytic Solution	Plating Conditions			
				Current Density : I_k (A/dm ²)	Flow Rate of Plating Solution: U (m/s)	$\frac{I_k}{U^{1/2}M}$	Plating Time (s)
23	Comparative Example 8	GA	Nickel Sulfate:	12	2	42	0.5
24	Example 16	GA	0.16 mol/l	15	2	53	0.5
25	Example 17	GA	Ferrous Sulfate	20	2	71	0.5
26	Example 18	GA	0.04 mol/l	25	2	88	0.5
27	Example 19	GA	pH: 2.8	30	2	106	0.5
28	Example 20	GA	Temperature:	40	2	141	0.5
29	Comparative Example 9	GA	50 °C	50	2	178	0.5
30	Comparative Example 10	GA	Nickel Sulfate:	50	2	16	0.5
31	Comparative Example 11	GA	1.76 mol/l	100	2	32	0.5
32	Comparative Example 12	GA	Ferrous Sulfate: 0.44 mol/l	150	2	48	0.5
33	Comparative Example 13	EG	pH: 2	-	-	-	-
34	Comparative Example 14	EG	Temperature: 50 °C	12	2	42	0.5
35	Example 21	EG	Nickel Sulfate:	15	2	53	0.5
36	Example 22	EG	0.16 mol/l	20	2	71	0.5
37	Example 23	EG	Ferrous Sulfate	25	2	88	0.5
38	Example 24	EG	0.04 mol/l	30	2	106	0.5
39	Example 25	EG	pH: 2.8	40	2	141	0.5
40	Comparative Example 15	EG	Temperature: 50 °C	50	2	178	0.5
41	Comparative Example 16	GI	Nickel Sulfate:	-	-	-	-
42	Comparative Example 17	GI	0.16 mol/l	8	1	40	1
43	Example 26	GI	Ferrous Sulfate	10	1	50	1
44	Example 27	GI	0.04 mol/l	16	1	80	1
45	Example 28	GI	pH: 1.5	20	1	100	1
46	Example 29	GI	Temperature:	24	1	120	1
47	Example 30	GI	50 °C	30	1	150	1
48	Comparative Example 18	GI		34	1	170	1

Note M: The sum of Ni ion concentration and ferrous ion concentration (mol/l)

On the Fe-Ni-O film of each specimen obtained in the above-described examples and comparative examples, the coating weight (in terms of the total weight of metals in the film), the ratio of the Fe content (% by weight) to the sum of the Fe content (% by weight) and the Ni content (% by weight), and the oxygen content were measured.

Tables 5 and 6 show the results of the above-described measurements performed on specimens obtained in Examples 1 through 30 and Comparative Examples 1 through 18.

Table 5

No	Test Sample	Type of Plating	Fe-Ni-O Film				Press-		Spot-Weldability	Adhesion Properties
			Coating Weight in Terms of Total Metal Weight (mg/m ²)	Fe Ratio Fe/Fe+Ni (%)	O ₂ Content (wt.%)	Friction Coefficient Bead A	Friction Coefficient Bead B			
1	Comparative Example 1	GA	0	-	-	0.171	0.255	2900	6.8	
2	Comparative Example 2	GA	40	0.28	0.20	0.148	0.173	4900	8.8	
3	Example 1	GA	56	0.29	0.50	0.125	0.151	5100	12.2	
4	Example 2	GA	82	0.29	1.00	0.127	0.150	5000	12.2	
5	Example 3	GA	120	0.30	4.00	0.125	0.151	5400	12.0	
6	Example 4	GA	140	0.30	6.00	0.126	0.150	5200	12.6	
7	Example 5	GA	182	0.29	9.00	0.125	0.147	5000	12.5	
8	Comparative Example 3	GA	200	0.27	12.00	0.128	0.152	4000	12.4	
9	Comparative Example 4	GA	90	0.25	0.30	0.146	0.169	5000	7.9	
10	Example 6	GA	110	0.26	0.60	0.124	0.148	5100	12.2	
11	Example 7	GA	170	0.26	1.20	0.124	0.148	5000	12.1	
12	Example 8	GA	260	0.26	5.00	0.124	0.146	5100	12.3	
13	Example 9	GA	310	0.25	6.80	0.126	0.145	5200	12.4	
14	Example 10	GA	390	0.24	9.50	0.125	0.144	4900	12.6	
15	Comparative Example 5	GA	420	0.24	13.00	0.126	0.142	3200	12.8	
16	Comparative Example 6	GA	220	0.28	0.30	0.145	0.165	5000	8.9	
17	Example 11	GA	250	0.28	0.60	0.122	0.142	5000	12.5	
18	Example 12	GA	430	0.26	1.30	0.123	0.142	5100	12.8	
19	Example 13	GA	640	0.25	6.20	0.124	0.143	5300	12.9	
20	Example 14	GA	760	0.27	7.00	0.123	0.140	5100	12.6	
21	Example 15	GA	1000	0.27	10.00	0.125	0.145	5000	12.8	
22	Comparative Example 7	GA	1100	0.28	15.00	0.124	0.145	3000	13.0	

Table 6

No	Test Sample	Type of Plating	Fe-Ni-O Film			Press-Moldability		Spot-Weldability Continuous Spot-Welding Runs	Adhesion Properties Peel Strength (kgf/25mm)
			Coating Weight in Terms of Total Metal Weight (mg/m ²)	Fe Ratio Fe/Fe-Ni (-)	O ₂ Content (wt. %)	Friction Coefficient Bead A	Friction Coefficient Bead B		
23	Comparative Example 8	GA	70	0.21	0.40	0.145	0.166	5200	7.7
24	Example 16	GA	88	0.20	0.60	0.121	0.142	5200	12.8
25	Example 17	GA	117	0.20	1.20	0.121	0.142	5100	13.0
26	Example 18	GA	148	0.21	5.80	0.122	0.146	5200	13.0
27	Example 19	GA	170	0.20	6.50	0.120	0.142	5100	13.0
28	Example 20	GA	240	0.20	9.20	0.123	0.145	5100	12.9
29	Comparative Example 9	GA	290	0.21	13.00	0.125	0.145	3200	13.2
30	Comparative Example 10	GA	220	0.28	0.10	0.154	0.174	5200	8.8
31	Comparative Example 11	GA	410	0.28	0.20	0.153	0.172	5100	9.0
32	Comparative Example 12	GA	600	0.29	0.40	0.152	0.171	5100	8.5
33	Comparative Example 13	EG	0	-	-	0.224	0.306	1900	5.6
34	Comparative Example 14	EG	80	0.27	0.30	0.147	0.167	4100	8.0
35	Example 21	EG	102	0.27	0.50	0.127	0.146	4200	12.2
36	Example 22	EG	120	0.26	1.00	0.125	0.145	4200	12.2
37	Example 23	EG	160	0.27	4.50	0.125	0.144	4200	12.2
38	Example 24	EG	190	0.26	6.00	0.124	0.145	4100	12.4
39	Example 25	EG	250	0.27	9.00	0.124	0.146	4200	12.4
40	Comparative Example 15	EG	310	0.29	16.00	0.125	0.147	2500	12.6
41	Comparative Example 16	GI	0	-	-	0.210	0.320	900	3.8
42	Comparative Example 17	GI	80	0.20	0.40	0.148	0.169	3500	7.6
43	Example 26	GI	100	0.21	0.60	0.125	0.149	3700	12.9
44	Example 27	GI	162	0.23	1.10	0.125	0.149	3800	12.9
45	Example 28	GI	240	0.21	5.00	0.126	0.147	3800	12.9
46	Example 29	GI	290	0.21	6.50	0.126	0.147	4000	12.5
47	Example 30	GI	365	0.23	9.50	0.128	0.147	4000	12.4
48	Comparative Example 18	GI	400	0.23	18.00	0.129	0.149	1500	12.4

Next, on each of the above specimens, measurement of the friction coefficient, tests on continuous spot-weldability and adhesiveness were conducted to evaluate press-formability, spot-weldability, and adhesiveness. The results are shown also in Tables 5 and 6.

The results shown in Tables 5 and 6 clarified the following.

Here, the left side of the equation $1, I_K/(U^{1/2}M) = 50$ through 150, is replaced with X. Specifically,

$$X = I_K / (U^{1/2} M) \quad (5)$$

As described above, only the X values are out of the scope of the present invention in the comparative examples, and:

- (1) In each of Comparative Examples 2, 4, 6, 8, 10 through 12, 14, and 17 which has an X value below 50, the oxygen content in the Fe-Ni-O film is less than 0.5 wt.% while that of each example is within a range of 0.1 through 10 wt.%. Additionally, these comparative examples are inferior to the examples based on the present invention in adhesiveness regardless of the type of plating layer. Further, the comparative examples are inferior to the examples based on the present invention having the same type of plating layer in press-formability;
- (2) In each of Comparative Examples 3, 5, 7, 9, 15, and 18 which has an X value exceeding 150, the oxygen content in the Fe-Ni-O film is greater than 10 wt.%. These comparative examples are inferior to the examples based on the present invention having the same type of plating layer in spot-weldability; and
- (3) All of Comparative Examples 1, 13 and 16, which were manufactured only by dipping in the electrolytic solution and have no Fe-Ni-O film, are inferior to the examples based on the present invention in all of press-formability, spot-weldability, and adhesiveness regardless of the type of plating layer.

As is obvious from Tables 5 and 6, the level of the characteristic values in press-formability, spot-weldability, and adhesiveness of the zinciferous plated steel sheets are dispersive in the products which were not subjected to the electrolytic treatment according to the present invention. Considering this, the characteristic values in Comparative Examples 1, 13, and 16, which were not subjected to the electrolytic treatment according to the present invention, are regarded as the standard values for the characteristic values of the products having plating layer of GA type, EG type, and GI type, respectively. Then, the ratio of each characteristic value in each of the examples based on the present invention and the other comparative examples to the standard value thus obtained was calculated and defined as the improvement index of each characteristic.

Tables 7 and 8 show the improvement indexes of press-formability, spot-weldability, and adhesiveness in the examples and the comparative examples, classifying them in terms of the type of plating layer.

Table 7

No	Test Sample	Type of Plating	Improvement Index of Press-formability		Improvement Index of Spot-Weldability	Improvement Index of Adhesion Properties
			Friction Coefficient		Continuous Spot-Welding runs	Peeloff Strength
			Bead A	Bead B		
1	Comparative Example 1	GA	1.000	1.000	1.000	1.000
2	Comparative Example 2	GA	0.865	0.768	1.690	1.294
3	Example 1	GA	0.731	0.592	1.759	1.794
4	Example 2	GA	0.743	0.588	1.724	1.794
5	Example 3	GA	0.731	0.592	1.862	1.764
6	Example 4	GA	0.737	0.588	1.793	1.853
7	Example 5	GA	0.731	0.576	1.724	1.838
8	Comparative Example 3	GA	0.749	0.596	1.379	1.824
9	Comparative Example 4	GA	0.854	0.663	1.724	1.162
10	Example 6	GA	0.725	0.580	1.759	1.794
11	Example 7	GA	0.725	0.580	1.724	1.779
12	Example 8	GA	0.725	0.573	1.759	1.809
13	Example 9	GA	0.737	0.569	1.793	1.824
14	Example 10	GA	0.731	0.565	1.690	1.853
15	Comparative Example 5	GA	0.737	0.557	1.103	1.882
16	Comparative Example 6	GA	0.848	0.647	1.724	1.309
17	Example 11	GA	0.713	0.557	1.724	1.838
18	Example 12	GA	0.719	0.557	1.759	1.882
19	Example 13	GA	0.725	0.561	1.828	1.897
20	Example 14	GA	0.719	0.549	1.759	1.853
21	Example 15	GA	0.731	0.569	1.724	1.883
22	Comparative Example 7	GA	0.725	0.569	1.034	1.912

Note: Each improvement index of press-moldability, spot-weldability, or adhesion properties is the ratio of each characteristic observed in an example to that of the corresponding comparative example having the same type of deposit as the example without a Fe-Ni-O-type coat.

Table 8

No	Test Sample	Type of Plating	Improvement Index of Press-formability		Improvement Index of Spot-weldability	Improvement Index of Adhesion Properties
			Friction Coefficient	Peeloff Strength		
23	Comparative Example 8	GA	0.847	0.651	1.793	1.000
24	Example 16	GA	0.708	0.557	1.793	1.662
25	Example 17	GA	0.708	0.557	1.759	1.688
26	Example 18	GA	0.713	0.573	1.793	1.688
27	Example 19	GA	0.702	0.557	1.759	1.688
28	Example 20	GA	0.719	0.568	1.759	1.675
29	Comparative Example 9	GA	0.731	0.568	1.103	1.714
30	Comparative Example 10	GA	0.901	0.682	1.793	1.294
31	Comparative Example 11	GA	0.895	0.675	1.759	1.324
32	Comparative Example 12	GA	0.889	0.671	1.759	1.250
33	Comparative Example 13	EG	1.000	1.000	1.000	1.000
34	Comparative Example 14	EG	0.656	0.546	2.158	1.429
35	Example 21	EG	0.567	0.477	2.211	2.179
36	Example 22	EG	0.558	0.474	2.211	2.179
37	Example 23	EG	0.558	0.471	2.211	2.179
38	Example 24	EG	0.554	0.474	2.158	2.214
39	Example 25	EG	0.554	0.477	2.211	2.214
40	Comparative Example 15	EG	0.558	0.480	1.315	2.250
41	Comparative Example 16	GI	1.000	1.000	1.000	1.000
42	Comparative Example 17	GI	0.705	0.528	3.889	2.000
43	Example 26	GI	0.595	0.466	4.111	3.395
44	Example 27	GI	0.595	0.466	4.222	3.395
45	Example 28	GI	0.600	0.459	4.222	3.395
46	Example 29	GI	0.600	0.459	4.444	3.289
47	Example 30	GI	0.610	0.459	4.444	3.263
48	Comparative Example 18	GI	0.614	0.466	1.667	3.263

Note: Each improvement index of press-moldability, spot-weldability, or adhesion properties is the ratio of each characteristic observed in an example to that of the corresponding comparative example having the same type of deposit as the example without a Fe-Ni-O-type coat.

As is obvious from the results shown in Tables 7 and 8, when press-formability, spot-weldability, and adhesiveness are evaluated in each group classified in terms of the type of plating layer, all of the examples based on the present invention are much more improved in each characteristic than in the comparative examples.

According to the present invention constructed as described above, the Fe-Ni-O film to be formed on the surface of the plating layer on a zinciferous plated steel sheet has a higher hardness and a higher melting point as compared with a zinc or alloyed zinc plating layer. With the presence of a proper amount of the film, the slide resistance between the surface of the plating layer and a press die during press forming decreases, and therefore, the zinciferous plated steel

sheet can readily flow into the mold. Also, the presence of the Fe-Ni-O film having a higher melting point improves continuous spot-weldability in spot-welding. Further, the peeloff strength of a laminated steel sheet can be improved due to the presence of Fe oxide in the Fe-Ni-O film. Accordingly, the present invention can provide a zinciferous plated steel sheet excellent in press-formability, spot-weldability, and adhesiveness, namely, the present invention can bring about markedly advantageous effects from an industrial view.

EMBODIMENT 3

The present invention provides a method of manufacturing a zinciferous plated steel sheet excellent in press formability, spot weldability and adhesiveness by appropriately forming an Fe-Ni-O film on the surface of a plating layer of the zinciferous plated steel sheet.

The method of manufacturing a zinciferous plated steel sheet of the present invention comprises the step of dipping a zinciferous plated steel sheet in an aqueous solution containing at least one of ferrous sulfate and ferrous nitrate and at least one of nickel sulfate and nickel nitrate, thereby forming a film on the surface of a plating layer of the zinciferous plated steel sheet, wherein the sum of the iron content (mol/l) and the nickel content (mol/l) in that aqueous solution is within a range of from 0.1 to 3.0 mol/l, the ratio of the iron content (mol/l) to the sum of the iron content (mol/l) and the nickel content (mol/l) in the aqueous solution is within a range of from 0.004 to 0.9, pH is within a range of from 1.0 to 3.5, and temperature is within a range of from 20 to 70 °C, and an Fe-Ni-O film is formed by dipping the zinciferous plated steel sheet in the aqueous solution.

In the present invention, the Fe-Ni-O film as an upper layer, formed on the surface of the plating layer of the zinciferous plated steel sheet of the present invention and in relation thereto shall be referred to as the "film," and on the other hand, the zinc or zinciferous plating layer as a lower layer shall be referred to as the "plating layer" for discrimination.

Now, reasons of limiting the manufacturing conditions in the present invention will be described below.

In the present invention, a zinciferous plated steel sheet is immersed in an aqueous solution containing at least one of FeSO_4 and $\text{Fe}(\text{NO}_3)_2$ and at least one of NiSO_4 and $\text{Ni}(\text{NO}_3)_2$ with a view to forming an Fe-Ni-O film on the surface of a plating layer of the zinciferous plated steel sheet. The reason is that Fe ion and Ni ion can be added to the solution in any of various forms of salt, but addition should be made in the form of a sulfate and/or nitrate because of the satisfactory solubility, a limited problem of corrosion of the facilities, the slight adverse effect on human health, and the favorable economic merits.

For the purpose of forming the Fe-Ni-O film, a spraying method of an aqueous film forming solution, or a roll-application method can give a similar effect as in the dipping method. However, an electroplating method results in a metallic film, and it is difficult to form the Fe-Ni-O film of the present invention, making it difficult to obtain a film excellent in press formability and adhesiveness. The electroplating method or the vapor plating method is not desirable in general because of the necessity of a huge amount of equipment cost and a high running cost leading to an increase in the manufacturing cost.

The sum of the iron content (mol/l) and the nickel content (mol/l) in the aqueous solution should be within a range of from 0.1 to 3.0. The reason is as follows. With a sum of under 0.1 mol/l, a decrease in the precipitation rate of Ni and Fe results in a decrease in productivity. With a sum of over 3.0, on the other hand, the metal salt concentration reaches the solubility at a low temperature, leading to precipitation of metal salts. In addition, the ratio of the Fe content (mol/l) to the sum of the Fe content (mol/l) and the Ni content (mol/l) in the aqueous solution should be within a range of from 0.004 to 0.9. The reason is that, with a ratio $\text{Fe}/(\text{Fe} + \text{Ni})$ of under 0.004, the improving effect of adhesiveness is unavailable, and with a ratio of over 0.9, the improvement effect of spot weldability is limited.

The aqueous solution should have a pH within a range of from 1.0 to 3.5. With a pH of under 1.0, there is an extreme increase in the amount of hydrogenation, resulting in a decrease in precipitation efficiency of Ni and Fe. Under conditions including constant salt concentration and dipping time, the coating weight of Ni and Fe is small, leading to a lower productivity. Furthermore, the film comprises mainly Ni and Fe metals, this making it impossible to obtain improving effect of press formability, spot weldability and adhesiveness. With a pH of over 3.5, the oxygen content in the film increases, resulting in a lower improving effect of weldability and in deterioration of chemical treatability.

Temperature of the aqueous solution should be within a range of from 20 to 70 °C. At a solution temperature of under 20 °C, the reaction rate is low and it takes a long period of time to ensure a sufficient coating weight of Ni and Fe necessary for improving film properties, resulting in a decrease in productivity. At a temperature of over 70 °C, on the other hand, deterioration of treatment performance of the aqueous solution is accelerated, and necessity of facilities and energy for keeping a high temperature results in an increase in the manufacturing cost.

The electrolytic solution may contain cations, hydroxides and oxides of Zn, Co, Mn, Mo, Al, Ti, Sn, W, Si, Pb, Nb and Ta contained in the plating layer or the like of the zinciferous plated steel sheet used in the present invention, and anions other than chlorine cation.

In the present invention, the zinciferous plated steel sheet used for forming the Fe-Ni-O film on the surface thereof is a steel sheet having a plating layer formed by the dip plating method, the electroplating method, the vapor plating method or the like on a substrate. In terms of chemical composition, the zinciferous plating layer comprises, in addition

to pure zinc, a single-layer or a plurality of layer plating layer containing one or more of such metals as Fe, Ni, Co, Mn, Cr, Al, Mo, Ti, Si, W, Sn, Pb, Nb and Ta (Si is also regarded as a metal), or oxides thereof, or organic substances. The layer may contain furthermore such fine particles as SiO_2 and Al_2O_3 . As the zinciferous plated steel sheet, a plurality of layers plated steel sheet or a functional gradient plated steel sheet having a plating layer with a different chemical composition may be used.

The Fe-Ni-O film formed on the surface of the plating layer of the zinciferous plated steel sheet under the foregoing limiting conditions eliminates sticking between the steel sheet and the die during press forming, reduces sliding resistance, improves flowing-in into the die, inhibits formation of a brittle alloy layer between the sheet and the copper electrode during spot welding, thus improving continuous spot weldability and improves adhesiveness under the effect of the film containing Fe oxides.

In this case, the coating weight of the Fe-Ni-O film should preferably be within a range of from 10 to 1,500 mg/m^2 in the total conversion weight of metal elements in the film. With a total conversion weight of under 10 mg/m^2 , the improving effect of press formability is unavailable, and a total conversion weight of over 1,500 mg/m^2 results in a deterioration of chemical treatability.

In order to adjust the coating weight within such a preferable range, it suffices, for an aqueous solution of a constant salt concentration, to adjust the dipping time, and when a constant dipping time must be kept because of restrictions in equipment such as capacity limit, to adjust the salt concentration, or finely adjust pH and temperature.

The preferable range of the oxygen content in the Fe-Ni-O film is from 0.5 to 10 wt.%. With an oxygen content of under 0.5 wt.%, metal properties of the film become more apparent, reducing the improving effect of press formability. With an oxygen content of over 10 wt.%, on the other hand, the amount of oxides becomes too large, resulting in an increase in electric resistance of the surface, a decrease in weldability, and inhibited production of phosphate crystals, leading to deterioration of chemical treatability.

The ratio of the Fe content (wt.%) to the sum of the Fe content and the Ni content in the film (wt.%) (hereinafter referred to as the "Fe ratio in film" and expressed by $\text{Fe}/(\text{Fe} + \text{Ni})$) should preferably be within a range of from 0.004 to 0.9, or more preferably, from 0.1 to 0.5. While presence of Fe in the film improves adhesiveness, a ratio $\text{Fe}/(\text{Fe} + \text{Ni})$ in the film of under 0.004, the improving effect of adhesiveness is unavailable. With a ratio $\text{Fe} / (\text{Fe} + \text{Ni})$ in the film of over 0.9, on the other hand, a decrease in the Ni content in the film results in a decrease in the ratio of Zn-Ni alloy having a high melting point formed during welding, and this causes more serious deterioration of the electrode, thus reducing the improving effect of spot weldability.

Examples

The zinciferous plated steel sheet before application of dip plating by the method of the present invention or a comparative method has any of the following plating seeds GA, GI, EG Zn-Fe, Zn-Ni, Zn-Cr and Zn-Al formed thereon:

GA: There is formed an alloyed zinc dip-plating layer comprising 10 wt.% Fe and the balance Zn in a coating weight of 60 g/m^2 for each of the both surfaces;

GI: There is formed a zinc dip-plating layer in a coating weight of 90 g/m^2 for each of the both surfaces;

EG: There is formed an electroplating layer in a coating weight of 40 g/m^2 for each of the both surfaces;

Zn-Fe: There is formed a Zn-Fe alloy electroplating layer comprising 15 wt.% Fe, in a coating weight 40 g/m^2 for each of the both surfaces;

Zn-Ni: There is formed a Zn-Ni alloy electroplating layer comprising 12 wt.% Ni, in a coating weight of 30 g/m^2 for each of the both surfaces;

Zn-Cr: There is formed a Zn-Cr alloy electroplating layer comprising 4 wt.% Cr, in a coating weight of 20 g/m^2 for each of the both surfaces;

Zn-Al: There is formed a Zn-Al alloy electroplating layer comprising 5 wt.% Al, in a coating weight of 60 g/m^2 for each of the both surfaces.

Examples of the invention and comparative examples were conducted by treating the foregoing zinciferous plated steel sheet under the manufacturing conditions within the scope of the present invention or manufacturing conditions outside the scope of the present invention shown in treatment Nos. 1 to 35 in Tables 9 and 10. Sample Nos. were assigned to samples determined by the combination of treatment conditions (treatment Nos. 1 to 35) and zinciferous plated steel sheets of any of the types of plating (7 types as above). The samples comprise examples Nos. 1 to 75 and comparative examples Nos. 1 to 31.

Table 9

Treatment No.	Aqueous Solution					pH	Temperature (°C)	Fe/(Fe+Ni)	Dipping Time (sec)	
	FeSO ₄ (mol/l)	Fe(NO ₃) ₂ (mol/l)	NiSO ₄ (mol/l)	Ni(NO ₃) ₂ (mol/l)						
1	-	-	-	-	-	-	-	-	-	Comparative Example
2	0.0000	0.0000	1.5000	0.0000	2.5	55	0.000	10	10	Comparative Example
3	0.0045	0.0000	1.4955	0.0000	2.5	55	0.003	10	10	Comparative Example
4	0.0060	0.0000	1.4940	0.0000	2.5	55	0.004	10	10	Example
5	0.0150	0.0000	1.4850	0.0000	2.5	55	0.010	10	10	Example
6	0.0750	0.0000	1.4250	0.0000	2.5	55	0.050	10	10	Example
7	0.1500	0.0000	1.3500	0.0000	2.5	55	0.100	10	10	Example
8	0.3000	0.0000	1.2000	0.0000	2.5	55	0.200	10	10	Example
9	0.4500	0.0000	1.0500	0.0000	2.5	55	0.300	10	10	Example
10	0.7500	0.0000	0.7500	0.0000	2.5	55	0.500	10	10	Example
11	1.0500	0.0000	0.4500	0.0000	2.5	55	0.700	10	10	Example
12	1.3500	0.0000	0.1500	0.0000	2.5	55	0.900	10	10	Example
13	1.3800	0.0000	0.1200	0.0000	2.5	55	0.920	10	10	Comparative Example
14	1.5000	0.0000	0.0000	0.0000	2.5	55	1.000	10	10	Comparative Example

Table 10

Treatment No.	Aqueous Solution					Dipping Time (sec)	
	FeSO ₄ (mol/l)	Fe(NO ₃) ₂ (mol/l)	NiSO ₄ (mol/l)	Ni(NO ₃) ₂ (mol/l)	pH	Temperature (°C)	Fe/(Fe+Ni)
15	0.3000	0.0000	1.2000	0.0000	0.5	55	0.200
16	0.3000	0.0000	1.2000	0.0000	0.9	55	0.200
17	0.3000	0.0000	1.2000	0.0000	1.0	55	0.200
18	0.3000	0.0000	1.2000	0.0000	1.5	55	0.200
19	0.3000	0.0000	1.2000	0.0000	2.0	55	0.200
20	0.3000	0.0000	1.2000	0.0000	2.1	55	0.200
21	0.3000	0.0000	1.2000	0.0000	3.0	55	0.200
22	0.3000	0.0000	1.2000	0.0000	3.5	55	0.200
23	0.3000	0.0000	1.2000	0.0000	3.6	55	0.200
24	0.3000	0.0000	1.2000	0.0000	4.0	55	0.200
25	0.3000	0.0000	1.2000	0.0000	2.5	10	0.200
26	0.3000	0.0000	1.2000	0.0000	2.5	19	0.200
27	0.3000	0.0000	1.2000	0.0000	2.5	20	0.200
28	0.3000	0.0000	1.2000	0.0000	2.5	40	0.200
29	0.3000	0.0000	1.2000	0.0000	2.5	50	0.200
30	0.3000	0.0000	1.2000	0.0000	2.5	60	0.200
31	0.3000	0.0000	1.2000	0.0000	2.5	70	0.200
32	0.3000	0.0000	1.2000	0.0000	2.5	71	0.200
33	0.3000	0.0000	1.2000	0.0000	2.5	80	0.200
34	0.1500	0.1500	0.6000	0.6000	2.5	55	0.200
35	0.0000	0.3000	0.0000	1.2000	2.5	55	0.200

Tables 11 to 15 show results of a state test of the Fe-Ni-O film formed on each sample and a property test of each sample.

Table 11

Sample No.	Type of Plating	Fe-Ni-O Film			Press Formability Frictional Coefficient	Weldability Continuous Spot Weldability	Adhesiveness Peel-off Strength (kgf/25mm)	Chemical Treatability	
		Coating Weight (mg/m ²)	Fe Ratio Fe/(Fe+Ni)	Oxygen (wt%)					
1	A	GA	-	-	0.160	3000	5.6	0	Comparative Example
2	A	GA	0.000	5.0	0.143	7000	4.0	0	Comparative Example
3	A	GA	0.003	4.5	0.143	7000	7.0	0	Comparative Example
4	A	GA	0.004	4.0	0.141	7000	10.0	0	Example
5	A	GA	0.010	3.5	0.140	7000	10.5	0	Example
6	A	GA	0.050	2.5	0.138	6750	11.0	0	Example
7	A	GA	0.100	2.0	0.136	6750	12.0	0	Example
8	A	GA	0.200	1.0	0.132	6500	13.5	0	Example
9	A	GA	0.300	1.0	0.134	6500	13.5	0	Example
10	A	GA	0.500	1.5	0.137	6000	13.5	0	Example
11	A	GA	0.700	2.5	0.138	5500	13.5	0	Example
12	A	GA	0.900	3.5	0.139	5000	13.5	0	Example
13	A	GA	0.920	4.0	0.140	3500	13.5	0	Comparative Example
14	A	GA	1.000	5.0	0.143	3000	13.5	0	Comparative Example

(Note) The plating weight is represented by the total conversion weight of metal elements in the film.

Table 12

Sample No.	Type of Plating	Fe-Ni-O Film			Press Formability Frictional Coefficient	Weldability Continuous Spot Weldability	Adhesivity Peeloff Strength (kgf/25mm)	Chemical Treatability	
		Coating Weight (mg/m ²)	Fe Ratio Fe/(Fe+Ni)	Oxygen (wt%)					
15 A	GA	20	0.200	0.2	0.152	5000	9.0	0	Comparative Example
16 A	GA	40	0.200	0.4	0.151	5200	9.5	0	Comparative Example
17 A	GA	60	0.200	0.5	0.142	5300	11.0	0	Example
18 A	GA	80	0.200	0.5	0.140	5500	12.0	0	Example
19 A	GA	150	0.200	0.8	0.138	6000	12.3	0	Example
20 A	GA	170	0.200	0.6	0.136	6200	12.3	0	Example
21 A	GA	260	0.200	5.0	0.130	6750	12.5	0	Example
22 A	GA	300	0.200	10.0	0.130	6000	11.0	0	Example
23 A	GA	320	0.200	20.0	0.130	4500	10.5	X	Comparative Example
24 A	GA	350	0.200	25.0	0.130	4000	10.0	X	Comparative Example
25 A	GA	6	0.200	1.0	0.150	3250	9.5	0	Comparative Example
26 A	GA	8	0.200	1.0	0.149	3500	9.8	0	Comparative Example
27 A	GA	20	0.200	1.0	0.142	5000	11.5	0	Example
28 A	GA	100	0.200	1.0	0.138	5250	12.5	0	Example
29 A	GA	180	0.200	1.0	0.135	5750	12.5	0	Example
30 A	GA	270	0.200	1.0	0.132	6500	12.5	0	Example
31 A	GA	320	0.200	1.0	0.131	7250	12.0	0	Example
32 A	GA	330	0.200	1.0	0.130	7250	11.5	0	Comparative Example
33 A	GA	420	0.200	1.0	0.130	7500	11.0	0	Comparative Example
34 A	GA	200	0.200	1.0	0.133	6000	13.0	0	Example
35 A	GA	180	0.200	1.0	0.134	6000	13.0	0	Example

(Note) The plating weight is represented by the total conversion weight of metal elements in the film.

Table 13

Sample No.	Type of Plating	Fe-Ni-O Film			Press Formability Frictional Coefficient	Weldability Continuous Spot Weldability	Adhesivity Peeloff Strength (kgf/25mm)	Chemical Treatability	
		Coating Weight (mg/m ²)	Fe Ratio Fe/(Fe+Ni)	Oxygen (wt%)					
1 B	GI	-	-	-	0.180	1000	2.9	0	Comparative Example
2 B	GI	330	0.000	5.0	0.162	5000	5.9	0	Comparative Example
4 B	GI	330	0.004	4.0	0.160	5000	10.1	0	Example
7 B	GI	330	0.100	2.0	0.157	4750	11.9	0	Example
8 B	GI	330	0.200	1.0	0.153	4500	12.4	0	Example
9 B	GI	330	0.300	1.0	0.155	4500	12.4	0	Example
10 B	GI	330	0.500	1.5	0.158	4000	12.4	0	Example
11 B	GI	330	0.700	2.5	0.159	3500	12.4	0	Example
12 B	GI	330	0.900	3.5	0.160	3000	12.4	0	Example
13 B	GI	330	0.920	4.0	0.162	1500	12.4	0	Comparative Example
34 B	GI	300	0.200	1.0	0.154	4500	12.1	0	Example
35 B	GI	270	0.200	1.0	0.155	4500	12.1	0	Example
1 C	EG	-	-	-	0.180	1500	2.9	0	Comparative Example
2 C	EG	330	0.000	5.0	0.163	5500	5.9	0	Comparative Example
4 C	EG	330	0.004	4.0	0.161	5500	10.9	0	Example
7 C	EG	330	0.100	2.0	0.155	5250	11.9	0	Example
8 C	EG	330	0.200	1.0	0.155	5000	12.4	0	Example
9 C	EG	330	0.300	1.0	0.157	5000	12.4	0	Example
10 C	EG	330	0.500	1.5	0.159	4500	12.4	0	Example
11 C	EG	330	0.700	2.5	0.161	4000	12.4	0	Example
12 C	EG	330	0.900	3.5	0.162	3500	12.4	0	Example
13 C	EG	330	0.920	4.0	0.164	2000	12.4	0	Comparative Example
34 C	EG	300	0.200	1.0	0.156	5000	12.1	0	Example
35 C	EG	270	0.200	1.0	0.157	5000	12.1	0	Example

(Note) The plating weight is represented by the total conversion weight of metal elements in the film.

Table 14

Sample No.	Type of plating	Fe-Ni-O Film			Press Formability Frictional Coefficient	Weldability Continuous Spot Weldability	Adhesivity Peel-off Strength (kgf/25mm)	Chemical Treatability	
		Coating Weight (mg/m ²)	Fe Ratio Fe/(Fe+Ni)	Oxygen (wt%)					
1 D	Zn-Fe	-	-	-	0.155	4000	5.7	0	Comparative Example
2 D	Zn-Fe	220	0.000	5.0	0.137	8000	4.1	0	Comparative Example
4 D	Zn-Fe	220	0.004	4.0	0.135	8000	10.9	0	Example
7 D	Zn-Fe	220	0.100	2.0	0.132	7750	12.1	0	Example
8 D	Zn-Fe	220	0.200	1.0	0.128	7500	13.6	0	Example
9 D	Zn-Fe	220	0.300	1.0	0.130	7500	13.6	0	Example
10 D	Zn-Fe	220	0.500	1.5	0.134	7000	13.6	0	Example
11 D	Zn-Fe	220	0.700	2.5	0.136	6500	13.6	0	Example
12 D	Zn-Fe	220	0.900	3.5	0.135	6000	13.6	0	Example
13 D	Zn-Fe	220	0.920	4.0	0.137	4500	13.6	0	Comparative Example
34 D	Zn-Fe	200	0.200	1.0	0.129	7500	13.3	0	Example
35 D	Zn-Fe	180	0.200	1.0	0.130	7500	13.3	0	Example
1 E	Zn-Ni	-	-	-	0.155	8000	5.7	0	Comparative Example
2 E	Zn-Ni	220	0.000	5.0	0.137	10000 or Greater	4.1	0	Comparative Example
4 E	Zn-Ni	220	0.004	4.0	0.134	10000 or Greater	10.1	0	Example
7 E	Zn-Ni	220	0.100	2.0	0.132	10000 or Greater	12.1	0	Example
8 E	Zn-Ni	220	0.200	1.0	0.128	10000 or Greater	13.6	0	Example
9 E	Zn-Ni	220	0.300	1.0	0.130	10000 or Greater	13.6	0	Example
10 E	Zn-Ni	220	0.500	1.5	0.133	10000 or Greater	13.6	0	Example
11 E	Zn-Ni	220	0.700	2.5	0.135	10000 or Greater	13.6	0	Example
12 E	Zn-Ni	220	0.900	3.5	0.136	10000 or Greater	13.6	0	Example
13 E	Zn-Ni	220	0.920	4.0	0.137	9000	13.6	0	Comparative Example
34 E	Zn-Ni	200	0.200	1.0	0.129	10000 or Greater	13.3	0	Example
35 E	Zn-Ni	180	0.200	1.0	0.130	10000 or Greater	13.3	0	Example

(Note) The plating weight is represented by the total conversion weight of metal elements in the film.

Table 15

Sample No.	Type of Plating	Fe-Ni-O Film			Press Formability Frictional Coefficient	Weldability Continuous Spot Weldability	Adhesivity Peeloff Strength (kgf/25mm)	Chemical Treatability	
		Coating Weight (mg/m ²)	Fe Ratio Fe/(Fe+Ni)	Oxygen (wt%)					
1 F	Zn-Cr	-	-	-	0.155	1500	5.7	0	Comparative Example
2 F	Zn-Cr	220	0.000	5.0	0.138	5500	4.1	0	Comparative Example
4 F	Zn-Cr	220	0.004	4.0	0.136	5500	10.8	0	Example
7 F	Zn-Cr	220	0.100	2.0	0.132	5250	12.1	0	Example
8 F	Zn-Cr	220	0.200	1.0	0.128	5000	13.6	0	Example
9 F	Zn-Cr	220	0.300	1.0	0.130	5000	13.6	0	Example
10 F	Zn-Cr	220	0.500	1.5	0.132	4500	13.6	0	Example
11 F	Zn-Cr	220	0.700	2.5	0.134	4000	13.6	0	Example
12 F	Zn-Cr	220	0.900	3.5	0.135	3500	13.6	0	Example
13 F	Zn-Cr	220	0.920	4.0	0.137	2000	13.6	0	Comparative Example
34 F	Zn-Cr	200	0.200	1.0	0.129	5000	13.3	0	Example
35 F	Zn-Cr	180	0.200	1.0	0.130	5000	13.3	0	Example
1 G	Zn-Al	-	-	-	0.180	1000	2.9	0	Comparative Example
2 G	Zn-Al	330	0.000	5.0	0.162	5000	5.9	0	Comparative Example
4 G	Zn-Al	330	0.004	4.0	0.160	5000	10.4	0	Example
7 G	Zn-Al	330	0.100	2.0	0.157	4750	11.9	0	Example
8 G	Zn-Al	330	0.200	1.0	0.153	4500	12.4	0	Example
9 G	Zn-Al	330	0.300	1.0	0.155	4500	12.4	0	Example
10 G	Zn-Al	330	0.500	1.5	0.158	4000	12.4	0	Example
11 G	Zn-Al	330	0.700	2.5	0.159	3500	12.4	0	Example
12 G	Zn-Al	330	0.900	3.5	0.160	3000	12.4	0	Example
13 G	Zn-Al	330	0.920	4.0	0.162	1500	12.4	0	Comparative Example
34 G	Zn-Al	300	0.200	1.0	0.154	4500	12.1	0	Example
35 G	Zn-Al	270	0.200	1.0	0.155	4500	12.1	0	Example

(Note) The plating weight is represented by the total conversion weight of metal elements in the film.

As a state test of the Fe-Ni-O film formed on each sample, the coating weight (mg/m²) as converted into a total weight of metals, the ratio of the Fe content (wt.%) to the sum of the Fe content (wt.%) and the Ni content (wt.%) in the film (Fe/(Fe + Ni)) and the oxygen content (wt.%) in the film were measured as follows.

[Measurement of coating weight of film as converted into total metal weight and Fe/(Fe + Ni) in film]

For the samples of plating types GI, EG, Zn-Cr, and Zn-Al, the coating weight of the Fe-Ni-O film as converted into a total weight of metal elements in the film and chemical composition were measured by dissolving the Fe-Ni-O film, together with the surface zinciferous plating layer thereunder, with diluted hydrochloric acid to cause peeling, and performing quantitative analysis of Fe and Ni by the ICP method. Then, the ratio Fe/(Fe + Ni) in the film was calculated.

For the samples of plating GA, Zn-Fe and Zn-Ni, it was difficult to completely separate the component elements in the upper Fe-Ni-O film from those of the lower plating layer by the ICP method, since the lower plating layer contained the component elements of the Fe-Ni-O film. Therefore, only component elements of the Fe-Ni-O film not contained in the lower plating layer were quantitatively analyzed by the ICP method. Further, after Ar ion sputtering, the chemical composition distribution of the individual component elements in the Fe-Ni-O film in terms of the depth of the plating layer was measured by repeating measurement of the individual component elements of the Fe-Ni-O film by the XPS method, starting from the film surface. In this measurement, the distance between the depth at which a component element of the Fe-Ni-O film not contained in the lower plating layer showed a maximum concentration and the position equal to a half the depth at which that element was no more detected was taken as the thickness of the Fe-Ni-O film. The coating weight of the Fe-Ni-O film as converted into a total weight of metal elements in the film and the chemical composition were calculated from the results of the ICP method and those of the XPS method. Then, the ratio Fe/(Fe + Ni) was calculated.

[Measurement of oxygen content in film]

The oxygen content in the film was determined from the result of analysis in the depth direction based on the Auger electron spectroscopy (AES).

Then, as a property test of each of the samples of the examples and the comparative examples, press formability, continuous spot weldability, adhesiveness and chemical treatability were tested.

[Chemical treatability]

The following test was carried out to evaluate chemical treatability.

Each sample was treated under ordinary conditions with the use of a dipping-type zinc phosphating solution for under-coating of automobile painting (Nihon Perkerizing Co. Ltd.), and a zinc phosphate film was formed on the surface thereof. Crystallization of the thus formed zinc phosphate film was observed through a scanning type electron microscope (SEM). As a result, cases in which a zinc phosphate film is normally formed are marked with ○, and cases in which a zinc phosphate film is not formed or gaps are produced in crystals, with X.

The results of the frictional coefficient, continuous spot weldability, peeloff strength and chemical treatability tests mentioned above are shown in Tables 11 to 15.

Tables 11 to 15 reveals the following findings.

Regarding properties of the samples (press formability, spot weldability and adhesiveness), comparison of the examples and the comparative examples suggests the following fact. In the examples, there is available improvement in all the foregoing properties as compared with the comparative examples not having an Fe-Ni-O film formed thereon (samples Nos. 1A; 1B; 1C; 1D; 1E; 1F and 1G), and improvement in at least one of the properties as compared with the comparative examples having an Fe-Ni-O film formed under conditions outside the scope of the present invention (2A, 3A, 13A, 14A, 15A, 16A, 23A, 24A, 25A, 26A; 2B, 13B; 2C, 13C; 2D, 13D; 2E, 13E; 2F, 13F; 2G, 13G), suggesting that the examples have more excellent properties in general.

In the comparative examples in which temperature of the aqueous treatment solution was high outside the scope of the present invention (32A, 33A), there was an increase in the manufacturing cost, although properties were excellent.

According to the present invention having the construction as described above, the Fe-Ni-O film formed on the surface of the plating layer of the zinciferous plated steel sheet has a higher hardness and a higher melting point than a zinc or zinc alloy plating layer. Presence of this film reduces sliding resistance between the plating layer surface and a press die during press forming of the zinciferous plated steel sheet, and enables the zinciferous plated steel sheet to easily flow into the die, thus improving press formability. The Fe-Ni-O film of a high melting point permits improvement of continuous spot weldability. Presence of Fe oxides in the Fe-Ni-O film improves peeloff strength of bonded substrates. According to the present invention, therefore, there is provided a zinciferous plated steel sheet excellent in press formability, spot weldability and adhesiveness, thus providing industrially very useful effects.

EMBODIMENT 4

The present inventors found the possibility of largely improving press formability, spot weldability and adhesiveness

by forming an appropriate Fe-Ni-O film on the surface of a plating layer of a zinciferous plated steel sheet, and subjecting, immediately before forming the Fe-Ni-O film, the zinciferous plated steel sheet to an alkaline treatment in an alkaline solution having a pH of at least 11 for a period of from 2 to 30 seconds.

The zinciferous plated steel sheet is inferior to the cold-rolled steel sheet in press formability because, under a high surface pressure, sticking takes place between zinc having a low melting point and the die, leading to an increase in sliding resistance. In order to avoid this inconvenience, it is effective to form a film having a higher hardness and a higher melting point than a zinc or zinc alloy plating layer on the surface of the plating layer of the zinciferous plated steel sheet, which reduces sliding resistance between the plating layer surface and the press die during press forming, and enables the zinciferous plated steel sheet to more easily flow into the press die, thus improving press formability.

The zinciferous plated steel sheet is inferior to the cold-rolled steel sheet in continuous spot weldability because, during welding, molten zinc comes into contact with the copper electrode and forms a brittle alloy layer which causes a more serious deterioration of the electrode. A method of forming a film having a high melting point on the surface of the plating layer is believed to be effective for the purpose of improving continuous spot weldability. To improve spot weldability of the zinciferous plated steel sheet, the present inventors found it particularly effective to form an Fe-Ni-O film as a result of studies on various films. Although the reason is not clear, conceivable causes are formation of Zn-Ni alloys of a high melting point through reaction of Ni and Zn, the high melting point of Ni oxide and the high electric conductivity of Ni oxide since it has semiconductor-like properties.

While the zinciferous plated steel sheet has been known to be inferior to the cold-rolled steel sheet in adhesiveness, the cause has not as yet been clarified. As a result of studies on the cause of this inferiority, the present inventors elucidated that adhesiveness was governed by the chemical composition of the oxide film on the surface of the steel sheet. More specifically, while the oxide film on the surface of the cold-rolled steel sheet mainly comprises Fe oxide, the film on the zinciferous plated steel sheet surface mainly comprises Zn oxide. Adhesiveness varies with the chemical composition of the oxide film: Zn oxide are inferior to Fe oxide in adhesiveness.

It is now possible therefore to improve adhesiveness by forming a film containing Fe oxide on the surface of the zinciferous plated steel sheet, as in the present invention.

The present invention was developed on the basis of the foregoing findings, and the method of manufacturing a zinciferous plated steel sheet of the present invention comprises the steps of subjecting a zinciferous plated steel sheet to an alkaline treatment in an alkaline solution for a period of from 2 to 30 seconds, and then subjecting the same to a film forming treatment for forming an Fe-Ni-O film on the surface of a zinciferous plating layer of the zinciferous plated steel sheet after the alkaline treatment, thereby improving the quality.

A preferable method of manufacturing a zinciferous plated steel sheet of the present invention comprises forming the Fe-Ni-O film by treating the alkali-treated zinciferous plated steel sheet in a aqueous solution containing ferrous chloride and nickel chloride and having a pH within a range of from 2.0 to 3.5 and a temperature within a range of from 20 to 70 °C.

A more preferable method of manufacturing a zinciferous plated steel sheet of the present invention comprises forming the Fe-Ni-O film by treating the alkali-treated zinciferous plated steel sheet in an aqueous solution containing ferrous chloride and nickel chloride, in which the ratio of the iron content (wt.%) to the sum of the iron content (wt.%) and the nickel content (wt.%) is within a range of from 0.004 to 0.9, pH is within a range of from 2.0 to 3.5, and temperature is within a range of from 20 to 70 °C.

In the present invention, the Fe-Ni-O film as an upper layer, formed on the surface of the plating layer of the zinciferous plated steel sheet of the present invention and in relation thereto shall be referred to as the "film," and on the other hand, the zinc or zinciferous plating layer as a lower layer shall be referred to as the "plating layer" for discrimination, not a "film."

Now, reasons of limiting the manufacturing conditions in the present invention will be described below.

The zinciferous plated steel sheet is treated in the alkaline solution for a period of from 2 to 30 seconds, and then the Fe-Ni-O film is formed on the surface of a plating layer of the zinciferous plated steel sheet. The reason is that the zinciferous plated steel sheet having the Fe-Ni-O film, more excellent in press formability than in a case without an alkaline treatment is available.

Fig. 6 is a graph illustrating the relationship between the coating weight of Ni onto the surface of the plating layer of the zinciferous plated steel sheet and the frictional coefficient observed in a press formability test of the zinciferous plated steel sheet while comparing cases with and without an alkaline treatment. It is clear from Fig. 6 that, as compared with the case without the treatment, the case with treatment in the alkaline solution results in a smaller value of frictional coefficient when the coating weight of Ni is kept constant, and is superior in press formability.

As the alkaline solution, an aqueous solution of one or more of alkaline chemicals such as NaOH, KOH, Na₂SO₄, Na₂PO₄, LiOH and MgOH can be used. The alkali concentration of the aqueous solution should have a pH of at least 10, and pH should more preferably be adjusted to at least 11. In this case, it suffices to set the concentration in general to about 5 to 50 g/l.

When the Fe-Ni-O film is formed after treating the zinciferous plated steel sheet in an acidic solution, while a slight improvement of press formability is available, the resultant steel sheet is inferior to that treated in an alkaline solution in

press formability, spot weldability and adhesiveness. This is due to the improvement of adhesiveness of the Fe-Ni-O film formed after treatment of the zinciferous plated steel sheet in the alkaline solution. The treatment in the acidic solution causes increase in the amount of an oxide film inevitably produced on the surface of the zinciferous plated steel sheet, and the foregoing effect is considered unavailable.

In this case, the Fe-Ni-O film is a mixture of Fe metal, Fe oxide, Ni metal and Ni oxide. There is no particular restrictions on the method for forming the film: it suffices to treat the sheet in an aqueous solution containing iron ion, nickel ion and an oxidizing agent, and applicable methods include the dipping method in the aqueous solution, the spraying method of the aqueous solution and the electroplating method. Further, the laser CVD, the optical CVD, the vacuum deposition, sputtering vapor deposition or other vapor plating method may also be applicable.

The foregoing aqueous solution for film forming may incidentally contain cations, hydroxides and oxides as well as anions of Zn, Co, Mn, Mo, Al, Ti, Sn, W, Si, Pb, Nb and Ta contained in the plating layer of the zinciferous plated steel sheet used in the present invention.

For the purpose of improving alkali treatability of the zinciferous plated steel sheet, a surfactant or the like may be added to the alkaline solution. Addition of an oxidizing agent however forms oxides on the surface of the zinciferous plated steel sheet, resulting in deterioration of adhesiveness of the Fe-Ni-O film. Addition of an oxidizing agent or the like is not therefore desirable.

An aqueous solution containing FeCl_2 and NiCl_2 can be used when forming the Fe-Ni-O film. For the supply of ferric ion and nickel ion, use of a metal salt of chloride gives a high precipitation efficiency. With the same salt concentration and treating time, therefore, there is available a larger coating weight of Ni and Fe as compared with nitrates and sulfates, thus permitting improvement of productivity.

Fig. 7 is a graph illustrating differences in the Ni coating weight among cases where the zinciferous plated steel sheet is dipped in a chloride bath, a sulfate bath or a nitrate bath as the treatment solution for the formation of the Fe-Ni-O film, where the ratio of Ni to Fe in the treatment solution is 90:10, and the sum of concentration is 100 g/l.

The aqueous solution for the formation of the film should preferably have a pH within a range of from 2.0 to 3.5. The reason is as follows.

With a pH of under 2.0, the amount of hydrogenation from the cathode becomes excessively larger, leading to a lower precipitation efficiency, and with the same salt concentration and treating time, the coating weight of Ni and Fe is reduced, resulting in a lower productivity. The film has come to mainly comprise Ni and Fe metals, and improving effect of press formability, spot weldability and adhesiveness is unavailable. With a pH of over 3.5, on the other hand, oxidation of Fe in the aqueous solution becomes violent, and sludge causes defects of the surface of the steel sheet.

Fig. 8 is a graph illustrating an example of Ni coating weight relative to the dipping time with a pH varying from 2.0 to 3.5, under conditions including a treatment bath temperature of 50 °C, an Ni to Fe concentration ratio in the treatment bath of 20:80, and a sum of concentration of 100 g/l.

Temperature of the aqueous solution should be within a range of from 20 to 70 °C.

At a solution temperature of under 20 °C, the reaction rate is low and it takes a long period of time to ensure a sufficient coating weight of Ni and Fe necessary for improving film properties, resulting in a decrease in productivity. At a temperature of over 70 °C, on the other hand, deterioration of treatment performance of the aqueous solution is accelerated, and necessity of facilities and energy for keeping a high temperature results in an increase in the manufacturing cost.

The ratio of the Fe content (wt.%) to the sum of the Fe content (wt.%) and the Ni content (wt.%) in the aqueous solution ($\text{Fe}/(\text{Fe} + \text{Ni})$) should preferably be within a range of from 0.004 to 0.9. The reason is as follows.

With a ratio $\text{Fe}/(\text{Fe} + \text{Ni})$ in the aqueous solution of under 0.004, the improving effect of adhesiveness is unavailable. With a ratio of over 0.9, on the other hand, the improving effect of spot weldability is reduced.

The zinciferous plated steel sheet used in the present invention suffices to be is a steel sheet having a plating layer formed by the dip plating method, the electroplating method, the vapor plating method or the like on a substrate. In terms of chemical composition, the zinciferous plating layer comprises, in addition to pure zinc, a single-layer or a plurality of layers containing one or more of such metals as Fe, Ni, Co, Mn, Cr, Al, Mo, Ti, Si, W, Sn, Pb, Nb and Ta (Si is also regarded as a metal), or oxides thereof, or organic substances. The layer may contain furthermore such fine particles as SiO_2 and Al_2O_3 . As the zinciferous plated steel sheet, a plated steel sheet having a plurality of layer or a functional gradient plated steel sheet having a plating layer with a different chemical composition may be used.

The Fe-Ni-O film formed on the surface of the plating layer of the zinciferous plated steel sheet under the foregoing limiting conditions eliminates sticking between the steel sheet and the die during press forming, reduces sliding resistance, improves flow-in into the die, inhibits formation of a brittle alloy layer between the sheet and the copper electrode during spot welding, thus improving continuous spot weldability and improves adhesiveness under the effect of the film containing Fe.

Examples

The zinciferous plated steel sheet before forming the Fe-Ni-O film by the method of the present invention or a com-

parative method has any of the following plating seeds A, B, C, D, E, F and G formed thereon:

A: There is formed an alloyed dip-plating layer comprising 10 wt.% Fe and the balance Zn in a coating weight of 60 g/m² for each of the both surfaces;

B: There is formed a dip-plating layer in a coating weight of 90 g/m² for each of the both surfaces;

C: There is formed an electroplating layer in a coating weight of 40 g/m² for each of the both surfaces;

D: There is formed a Zn-Fe alloy electroplating layer comprising 15 wt.% Fe and the balance Zn, in a coating weight 40 g/m² for each of the both surfaces;

E: There is formed a Zn-Ni alloy electroplating layer comprising 12 wt.% Ni and the balance Zn, in a coating weight of 30 g/m² for each of the both surfaces;

F: There is formed a Zn-Cr alloy electroplating layer comprising 4 wt.% Cr and the balance Zn, in a coating weight of 20 g/m² for each of the both surfaces;

G: There is formed a Zn-Al alloy electroplating layer comprising 5 wt.% Al and the balance Zn, in a coating weight of 60 g/m² for each of the both surfaces.

Tests were carried out for examples in which the Fe-Ni-O film forming treatment was applied within the scope of the present invention to the above-mentioned zinciferous plated steel sheets, and for comparative examples in which the film forming treatment was not applied and comparative examples in which a method outside the scope of the present invention was applied.

Example 1.

A test was carried out, in which the plating type was fixed to symbol A (alloyed dip-plating), and conditions for alkali treatment as a pre-treatment and the method for forming the Fe-Ni-O film were altered.

Table 16 shows conditions for the tests Nos. 1 to 21 in detail. The solution for forming the Fe-Ni-O film was an aqueous solution containing FeCl₂ and NiCl₂.

Table 16

No	Test	Type of Plating	Alkali Treatment Condition				Fe-Ni-O Film		
			Solution		Treatment	Temperature (C°)	Time (sec)	Presence	Film Forming
			Chemical Composition	pH					
1	Comparative Example 1	A	-	-	-	-	-	X	-
2	Comparative Example 2	A	NaOH	12.0	Dipping	50	5	X	-
3	Comparative Example 3	A	-	-	-	-	-	O	Dipping
4	Comparative Example 4	A	NaOH	9.5	Dipping	50	5	O	Dipping
5	Example 1	A	NaOH	10.5	Dipping	50	5	O	Dipping
6	Example 2	A	NaOH	11.0	Dipping	50	5	O	Dipping
7	Example 3	A	NaOH	11.5	Dipping	50	5	O	Dipping
8	Example 4	A	NaOH	12.0	Dipping	50	5	O	Dipping
9	Example 5	A	NaOH	13.0	Dipping	50	5	O	Dipping
10	Example 6	A	NaOH	14.0	Dipping	50	5	O	Dipping
11	Comparative Example 5	A	H ₂ SO ₄	2.0	Dipping	50	5	O	Dipping
12	Comparative Example 6	A	HCl	2.0	Dipping	50	5	O	Dipping
13	Example 7	A	NaOH	12.0	Spray	50	5	O	Dipping
14	Example 8	A	KOH	12.0	Dipping	50	5	O	Dipping
15	Example 9	A	Na ₂ SiO ₄	12.0	Dipping	50	5	O	Dipping
16	Example 10	A	Mg(OH) ₂	12.0	Dipping	50	5	O	Dipping
17	Example 11	A	LiOH	12.0	Dipping	50	5	O	Dipping
18	Example 12	A	Na ₂ PO ₄	12.0	Dipping	50	5	O	Dipping
19	Example 13	A	NaOH	12.0	Dipping	50	5	O	Spray
20	Example 14	A	NaOH	12.0	Dipping	50	5	O	Electrolysis
21	Example 15	A	NaOH	12.0	Dipping	50	5	O	Vapor Deposition

O: With Fe-Ni-O film X: Without Fe-Ni-O film

45 Example 2

Tests were carried out on zinciferous plated steel sheets of plating type symbols B, C, D, E, F and G. Comparative examples included cases where an alkali treatment as a pre-treatment was not applied without applying the Fe-Ni-O film forming treatment, and cases with the alkali treatment but without the Fe-Ni-O film forming treatment. Examples covered cases where the Fe-Ni-O film forming treatment was applied after the alkali treatment. Alkali treatment conditions were the same for the comparative examples and the examples.

Table 17 shows details of conditions for tests Nos. 22 to 39. The solution for forming the Fe-Ni-O film had the same chemical composition as in Test 1.

Table 17

No	Test	Type of Plating	Alkali Treatment Condition					Fe-Ni-O Film	
			Solution		Treat-ment	Tempera-ture (°C)	Time (sec)	Pres-ence	Film Forming
			Chemical Compo-sition	pH					
22	Comparative Example 7	B	-	-	-	-	-	X	-
23	Comparative Example 8	B	NaOH	12.0	Dipping	50	5	X	-
24	Example 16	B	NaOH	12.0	Dipping	50	5	O	Dipping
25	Comparative Example 9	C	-	-	-	-	-	X	-
26	Comparative Example 10	C	NaOH	12.0	Dipping	50	5	X	-
27	Example 17	C	NaOH	12.0	Dipping	50	5	O	Dipping
28	Comparative Example 11	D	-	-	-	-	-	X	-
29	Comparative Example 12	D	NaOH	12.0	Dipping	50	5	X	-
30	Example 18	D	NaOH	12.0	Dipping	50	5	O	Dipping
31	Comparative Example 13	E	-	-	-	-	-	X	-
32	Comparative Example 14	E	NaOH	12.0	Dipping	50	5	X	-
33	Example 19	E	NaOH	12.0	Dipping	50	5	O	Dipping
34	Comparative Example 15	F	-	-	-	-	-	X	-
35	Comparative Example 16	F	NaOH	12.0	Dipping	50	5	X	-
36	Example 20	F	NaOH	12.0	Dipping	50	5	O	Dipping
37	Comparative Example 17	G	-	-	-	-	-	X	-
38	Comparative Example 18	G	NaOH	12.0	Dipping	50	5	X	-
39	Example 21	G	NaOH	12.0	Dipping	50	5	O	Dipping

O: With Fe-Ni-O film X: Without Fe-Ni-O film

Example 3

Tests were carried out with a fixed plating type symbol A and constant alkali treatment conditions for pre-treatment by altering the chemical composition of the Fe-Ni-O film forming solution. The aqueous solution contained FeCl_2 and NiCl_2 . The concentration of FeCl_2 and NiCl_2 was altered. The ratio of the Fe content (wt.%) to the sum of the Fe content (wt.%) and the Ni content (wt.%) was altered. The other conditions were kept constant.

Table 18 shows details of the conditions for tests Nos. 40 to 58.

Table 18

No	Test	Alkali Treatment Condition				Fe-Ni-O Film Forming Condition							
		Solution		Treat- ment	Tempera- ture (°C)	Time (sec)	Aqueous Solution						
		Chemical Compo- sition	pH				Film Forming	FeCl ₂ g/l	NiCl ₂ g/l	pH	Tempera- ture (°C)	Fe/ (Fe+Ni)	
				Time (s)									
40.	Comparative Example 19	A	NaOH	12.0	Dipping	5	Dipping	0	200.0	2.5	50	0	10
41.	Example 22	A	NaOH	12.0	Dipping	5	Dipping	0.7	199	2.5	50	0.0035	10
42.	Example 23	A	NaOH	12.0	Dipping	5	Dipping	0.8	199	2.5	50	0.004	10
43.	Example 24	A	NaOH	12.0	Dipping	5	Dipping	1.0	199	2.5	50	0.005	10
44.	Example 25	A	NaOH	12.0	Dipping	5	Dipping	5.0	195	2.5	50	0.025	10
45	Example 26	A	NaOH	12.0	Dipping	5	Dipping	10.0	190	2.5	50	0.05	10
46	Example 27	A	NaOH	12.0	Dipping	5	Dipping	20.0	180	2.5	50	0.1	10
47	Example 28	A	NaOH	12.0	Dipping	5	Dipping	30.0	170	2.5	50	0.15	10
48	Example 29	A	NaOH	12.0	Dipping	5	Dipping	40.0	160	2.5	50	0.2	10
49	Example 30	A	NaOH	12.0	Dipping	5	Dipping	50.0	150	2.5	50	0.25	10
50	Example 31	A	NaOH	12.0	Dipping	5	Dipping	60.0	140	2.5	50	0.3	10
51	Example 32	A	NaOH	12.0	Dipping	5	Dipping	80.0	120	2.5	50	0.4	10
52	Example 33	A	NaOH	12.0	Dipping	5	Dipping	100.0	100	2.5	50	0.5	10
53	Example 34	A	NaOH	12.0	Dipping	5	Dipping	120.0	80	2.5	50	0.6	10
54	Example 35	A	NaOH	12.0	Dipping	5	Dipping	140.0	60	2.5	50	0.7	10
55	Example 36	A	NaOH	12.0	Dipping	5	Dipping	160.0	40	2.5	50	0.8	10
56	Example 37	A	NaOH	12.0	Dipping	5	Dipping	180.0	20	2.5	50	0.9	10
57	Example 38	A	NaOH	12.0	Dipping	5	Dipping	185.0	15	2.5	50	0.925	10
58	Comparative Example 20	A	NaOH	12.0	Dipping	5	Dipping	200.0	0	2.5	50	1	10

For the samples of zinciferous plated steel sheets thus manufactured in Examples and Comparative Examples, evaluation tests of press formability, spot weldability, adhesiveness and chemical treatability were carried out. Spot weldability was evaluated in terms of the continuous spot welding runs. Adhesiveness was evaluated in terms of peeloff strength after bonding. Chemical treatability was evaluated in terms of the state of crystallization of the zinc phosphate

film.

Tables 19, 20 and 21 show the results of Tests 1, 2 and 3, respectively.

Table 19

No.	Test	Press Formability Frictional Coefficient (μ)	Spot Weldability Continuous Spot Weldability	Adhesiveness Peeloff strength (kgf/cm ²)	Chemical Treatability Condition of Zinc Phosphate Film
1	Comparative Example 1	0.150	2500	8.0	=
2	Comparative Example 2	0.145	2500	10.0	=
3	Comparative Example 3	0.125	5000	12.0	0
4	Comparative Example 4	0.125	5000	12.0	0
5	Example 1	0.120	5500	12.0	0
6	Example 2	0.115	5500	12.5	0
7	Example 3	0.110	5500	12.5	0
8	Example 4	0.110	5500	12.5	0
9	Example 5	0.105	5500	12.5	0
10	Example 6	0.105	5500	12.5	0
11	Comparative Example 5	0.130	5000	12.5	0
12	Comparative Example 6	0.130	5000	12.5	0
13	Example 7	0.110	5300	12.5	0
14	Example 8	0.110	5500	12.5	0
15	Example 9	0.110	5500	12.5	0
16	Example 10	0.110	5500	12.5	0
17	Example 11	0.110	5500	12.5	0
18	Example 12	0.110	5500	12.5	0
19	Example 13	0.110	5500	12.5	0
20	Example 14	0.110	5500	12.5	0
21	Example 15	0.110	5500	12.5	0
22	Comparative Example 7	0.180	1500	5.0	0
23	Comparative Example 8	0.175	1500	6.0	0
24	Example 16	0.130	4000	12.5	0
25	Comparative Example 9	0.180	2500	6.0	0
26	Comparative Example 10	0.175	250	7.0	0
27	Example 17	0.130	5000	12.5	0

Table 20

No.	Test	Press Formability Frictional Coefficient (μ)	Spot Weldability Continuous Spot Weldability	Adhesiveness Peeloff strength (kgf/cm ²)	Chemical Treatability Condition of Zinc Phosphate Film
28	Comparative Example 11	0.150	3000	8.0	O
29	Comparative Example 12	0.145	3000	10.0	O
30	Example 18	0.115	6000	12.0	O
31	Comparative Example 13	0.150	8000	6.0	O
32	Comparative Example 14	0.145	8000	7.0	O
33	Example 19	0.115	10000	12.5	O
34	Comparative Example 15	0.150	3000	6.0	O
35	Comparative Example 16	0.145	3000	7.0	O
36	Example 20	0.115	6000	12.5	O
37	Comparative Example 17	0.180	1500	5.0	O
38	Comparative Example 18	0.175	1500	7.0	O
39	Example 21	0.130	4000	12.5	O

Table 21

No.	Test	Press Formability Frictional Coefficient (μ)	Spot Weldability Continuous Spot Weldability	Adhesiveness Peeloff strength (kgf/cm ²)	Chemical Treatability Condition of Zinc Phosphate Film
40	Comparative Example 19	0.135	5500	6.0	0
41	Example 22	0.130	5500	11.0	0
42	Example 23	0.120	5500	12.0	0
43	Example 24	0.110	5500	12.5	0
44	Example 25	0.110	5500	12.5	0
45	Example 26	0.110	5500	12.5	0
46	Example 27	0.110	5000	12.5	0
47	Example 28	0.110	5000	12.5	0
48	Example 29	0.110	5500	12.5	0
49	Example 30	0.110	5500	12.5	0
50	Example 31	0.110	5500	12.5	0
51	Example 32	0.110	5500	12.5	0
52	Example 33	0.110	5500	12.5	0
53	Example 34	0.110	5500	12.5	0
54	Example 35	0.110	5000	12.5	0
55	Example 36	0.120	4500	12.5	0
56	Example 37	0.120	4000	12.5	0
57	Example 38	0.130	3500	12.5	0
58	Comparative Example 20	0.135	2500	12.5	0

Test result 1

From the result shown in Table 19, the following fact is evident.

When the plating type is fixed as symbol A (alloyed dip-plating), the Comparative Examples were inferior to the Examples in at least one of properties.

More specifically, (1) Comparative Example 1 in which an alkali treatment nor formation of an Fe-Ni-O film was conducted, and in Comparative Example 2 in which an alkali treatment was applied without however formation of an Fe-Ni-O film, are inferior to Examples in all of press formability, spot weldability, adhesiveness and chemical treatability.

(2) Comparative Example 3 with formation of an Fe-Ni-O film but not an alkali treatment is inferior to Examples in press formability.

(3) Comparative Example 4 in which the sheet was treated in an aqueous solution having an alkali concentration of pH: 9.5 which is lower than the concentration usually used for conventional alkali treatment and then an Fe-Ni-O film was formed was inferior to Examples in press formability.

(4) Comparative Examples 5 and 6 in which an Fe-Ni-O film was formed but a pre-treatment was conducted in an acidic solution are inferior to Examples in press formability.

Test result 2

The results shown in Table 5 suggest the following fact.

(1) For a primer plating type symbol D, E or F, even without an alkali treatment and formation of an Fe-Ni-O film, or with an alkali treatment but without formation of an Fe-Ni-O film, properties show values almost at the same level as under the same conditions with plating type symbol A. In the case of symbols B, C and G, however, Comparative examples 7, 9 and 17 without an alkali treatment nor formation of an Fe-Ni-O film, and Comparative Examples 8,

10 and 18 with an alkali treatment but without formation of an Fe-Ni-O film are further inferior even to Comparative Examples 1 and 2 of plating type symbol A under the same conditions in any of press formability, spot weldability and adhesiveness.

(2) Among cases with any of primer plating type symbols B, C, D, E, F and G, while Comparative Examples 7 to 18 are inferior in at least one of press formability, spot weldability and adhesiveness, Examples 17 to 21 show improved properties as compared with Comparative Examples of the same plating types.

Test result 3

From the result shown in Table 21, the following fact is clear for cases with plating type symbol A.

(1) Comparative Example 19 in which the zinciferous plated steel sheet was alkali-treated in an aqueous solution containing NiCl_2 but not FeCl_2 and then a film was formed, and Comparative Example 20 in which the sheet was treated in an aqueous solution containing FeCl_2 but not NiCl_2 are poor in press formability and adhesiveness, and in press formability and spot weldability, respectively.

(2) Examples 22 to 38 within the scope of the present invention show in contrast improvement in all of press formability, spot weldability, adhesiveness and chemical treatability. This improvement is particularly remarkable in cases where the ratio $\text{Fe (wt.%)}/(\text{Fe (wt.%) + Ni (wt.%)})$ in the Fe-Ni-O film treating solution is within a range of from 0.004 to 0.9.

Even in cases with plating type symbols B, C, D, E, F and G, results similar to those with plating type symbol A would be obtained.

According to the present invention having the construction as described above, the Fe-Ni-O film formed on the surface of the plating layer of the zinciferous plated steel sheet has a higher hardness and a higher melting point than a zinc or zinc alloy plating layer. Presence of this film reduces sliding resistance between the plating layer surface and a press die during press forming of the zinciferous plated steel sheet, and enables the zinciferous plated steel sheet to easily slip into the die, thus improving press formability. The Fe-Ni-O film of a high melting point permits improvement of continuous spot weldability. Presence of Fe oxides in the Fe-Ni-O film improves peeloff strength of bonded substrates. According to the present invention, therefore, there is provided a method of manufacturing a zinciferous plated steel sheet excellent in press formability, spot weldability and adhesiveness, thus providing industrially very useful effects.

EMBODIMENT 5

It was found that the formation of an island-like or mosaic Fe-Ni-O film on a surface of a zinciferous plating layer of a zinciferous plated steel sheet can improve press formability, spot weldability and adhesiveness.

A conventional zinciferous plated steel sheet is inferior to a cold-rolled steel sheet in press formability. This is caused by the increase in sliding resistance due to the adhesion of low-melting-point zinc to a die. In order to prevent this, it is effective to form a film having higher hardness and a higher melting point than a zinc or zinc alloy plating layer on the surface of the zinciferous plated steel sheet. Since the Fe-Ni-O film has high hardness and a high melting point, the formation of the island-like or mosaic-shaped Fe-Ni-O film on the surface of the zinciferous plated steel sheet decreases the sliding resistance between the deposit surface and the press die during press forming, and facilitates sliding of the zinciferous plated steel sheet into the press die, thereby improving the press formability.

A conventional zinciferous plated steel sheet is inferior to a cold-rolled steel sheet in the continuous spot weldability in spot welding. This is caused by the fact that a brittle alloy layer is formed due to melting of zinc and copper of an electrode in contact therewith during welding, thereby significantly deteriorating the electrode. In the present invention, therefore, since the island-like or mosaic Fe-Ni-O film is formed, a decrease in the contact area between the copper electrode and zinc during spot welding contributes to improvement in the spot weldability.

It is also thought that an effective method for improving the continuous spot weldability of the zinciferous plated steel sheet is to form a high-melting-point film on the surface of the plating layer. As a result of research on various films for improving the spot weldability of the zinciferous plated steel sheet, the inventors found that a Ni or Ni oxide film is particularly effective. Although the reasons for this are not apparent, a possible reason is that, since a high-melting-point Zn-Ni alloy is formed by reaction of Ni and Zn, Ni and Ni oxide have very high melting points, and the Ni oxide has semiconductor properties, the electric conductivity is high among the various films.

Although it is known that a conventional zinciferous plated steel sheet is inferior to a cold-rolled steel sheet in adhesiveness, the reasons for this are not apparent. As a result of examination of the reasons, therefore, the inventors found that the adhesiveness is governed by the composition of an oxide film on the steel surface. Namely, although the oxide film on the surface of the cold-rolled steel sheet is mainly composed of Fe oxide, the oxide film on the zinciferous plated steel sheet is mainly composed of Zn oxide. The adhesiveness depends upon the composition of the oxide film, and the

Zn oxide is inferior to the Fe oxide in adhesiveness. Therefore, the formation of a film containing a Fe oxide on the surface of the zinciferous plated steel sheet can improve the adhesiveness, as in the present invention.

The reasons why a conventional zinciferous plated steel sheet is inferior to a cold-rolled steel sheet in the chemical treatability are that, since the Zn content in the surface of the zinciferous plated steel sheet is high, the crystal structure of the formed phosphate film is coarse and nonuniform, and that the phosphate film on the zinciferous plated steel sheet has a crystal structure and a composition different from those of the cold-rolled steel sheet. When the Zn content in the surface of the steel sheet is high, the phosphate crystal mainly comprises hopeite, and the hot-water secondary adhesiveness after painting is poor. The cause of this is that, since the Fe content of the phosphate film is low, the adhesion force of the chemically-treated film to the steel sheet is lost due to condensation when the film is exposed to a wet environment after painting.

In order to prevent the chemically-treated film from recovering the lost water, it is effective to contain a metal such as Fe or Ni in the phosphate crystal. In the present invention, the formation of the Fe-Ni-O film causes Ni and Fe in the film to be captured in the phosphate crystal during chemical treatment to form a chemically treated film having good adhesiveness. Since the Fe-Ni-O film having an island-like or mosaic distribution is formed, the film does not cover the entire zinciferous plating layer. Therefore, at the same time, direct reaction of the chemically treated film and the zinciferous plating layer takes place, thereby ensuring the adhesive force for the zinciferous plating layer itself.

As described above, it was found that, when the mixed film comprising Ni and Fe metals and oxides thereof, i.e., the Fe-Ni-O film, having an island-like or mosaic distribution is formed on the surface of the zinciferous plated steel sheet, the steel sheet obtained is excellent in all the press formability, spot weldability, adhesiveness and chemical treatability.

The present invention has been achieved on the basis of the above finding, and a zinciferous plated steel sheet of the present invention comprises a Fe-Ni-O film formed on at least one plating layer, wherein the Fe-Ni-O film has an island-like or mosaic distribution, the coating weight of the Fe-Ni-O film is within the range of 10 to 1500 mg/m² in terms of the total weight of the metal elements in the Fe-Ni-O film, and the ratio of surface coating of the Fe-Ni-O film is within the range of 30 to 90 %.

In the zinciferous plated steel sheet, the ratio of the Fe content (wt%) to the total of the Fe content (wt%) and the Ni content (wt%) of the Fe-Ni-O film is preferably within the range of 0.004 to 0.9, and the oxygen content of the Fe-Ni-O film is within the range of 0.5 to 10 wt%.

A method of producing a zinciferous plated steel sheet of the present invention comprises spraying a mist solution containing Fe ion and Ni ion and having a pH within the range of 1 to 3.5 on at least one plating layer of the zinciferous plated steel sheet, maintaining the zinciferous plated steel sheet at a temperature within the range of 20 to 70 °C for 1 second or more, and then heating the zinciferous plated steel sheet to form, on the plating layer, a Fe-Ni-O film having a coating weight within the range of 10 to 1500 mg/m² in terms of the total weight of metal elements, a rate of coating within the range of 30 to 90%, and an island-like or mosaic distribution.

In the method of producing a zinciferous plated steel sheet, the ratio of the Fe content (g/l) to the total of the Fe content (g/l) and the Ni content (g/l) in the mist solution is within the range of 0.004 to 0.9.

In the method of producing a zinciferous plated steel sheet, the Fe-Ni-O film is formed by heat treatment of the zinciferous plated steel sheet at a temperature of 80 to 500 °C.

Another method of producing a zinciferous plated steel sheet of the present invention is described below.

The important characteristic lies in the island-like or mosaic Fe-Ni-O film formed on the plating layer of the predetermined zinciferous plated steel sheet, and the forming method thereof. In order to properly form the island-like or mosaic Fe-Ni-O film, the zinciferous plated steel sheet is pre-treated as described below so as to form minute portions where the Fe-Ni-O film is easily formed, and minute portions where the Fe-Ni-O film is hardly formed on the plating layer. The Fe-Ni-O film is then formed on the zinciferous plated steel sheet with the surface having such minute portions formed thereon. The method of forming the film is characterized in that the coating weight is within the range of 10 to 1500 mg/m² in terms of the total weight of the metallic elements, and the ratio of coating is within the range of 30 to 90%.

The methods of pre-treating the zinciferous plated steel sheet include the following methods:

(1) Fine irregularities are formed on the surface of the plating layer by temper-rolling the zinciferous plated steel sheet.

(2) A new surface is formed on the surface of the plating layer by temper-rolling the zinciferous plated steel sheet.

(3) The air oxide film existing on the surface of the plating layer is partly dissolved by dipping the zinciferous plated steel sheet in an acid solution, or anodic electrolysis in an acid solution to form active and inactive portions on the surface of the plating layer.

(4) The air oxide film existing on the surface of the plating layer is partly dissolved by dipping the zinciferous plated steel sheet in an alkaline solution, or anodic electrolysis in an alkaline solution to form active and inactive portions on the surface of the plating layer.

In the method of producing a zinciferous plated steel sheet in accordance with any one of the above mentioned pre-treating methods (1) to (4), a cathodic electrolysis method is preferably used as the method of forming the Fe-Ni-O film, and the electrolytic solution used preferably satisfies conditions in that it contains nickel sulfate, ferrous sulfate and ferric sulfate in a total amount within the range of 0.3 to 2.0 mol/l, and the pH is within the range of 1 to 2.

In the method of producing a zinciferous plated steel sheet, the electrolytic solution used satisfies conditions in that the ratio of the Fe content (g/l) to the total of the Fe content (g/l) and the Ni content (g/l) is within the range of 0.004 to 0.9, and the molar ratio of ferric sulfate (mol/l) to the total of ferrous sulfate (mol/l) and ferric sulfate (mol/l) is within the range of 0.5 to less than 1.0.

In the method of producing a zinciferous plated steel sheet in accordance with any one of the above mentioned pre-treating methods (1) to (4), an aqueous solution is used for forming the Fe-Ni-O film, and the aqueous solution contains FeCl_2 and NiCl_2 , and satisfies conditions in that the pH is within the range of 2.0 to 3.5, and the temperature is within the range of 20 to 70 °C.

In the method of producing a zinciferous plated steel sheet, the aqueous solution used for forming the Fe-Ni-O film satisfies a condition in that the ratio of the Fe content (g/l) to the total of the Fe content (g/l) and the Ni content (g/l) is within the range of 0.004 to 0.9.

Fig. 9 is a schematic drawing illustrating a longitudinal section of a zinciferous plated steel sheet in accordance with an embodiment of the present invention. As shown in the drawing, the zinciferous plated steel sheet of the present invention comprises a steel sheet 21, a zinciferous plating layer 22 formed on at least one surface of the steel sheet 21, and a Fe-Ni-O film 23 formed on the surface of the zinciferous plating layer 22 and having an island-like or mosaic distribution.

The reasons for limiting the Fe-Ni-O film of the zinciferous plated steel sheet as described above are described below.

The reasons for determining the coating weight of the Fe-Ni-O film to 10 to 1500 mg/m^2 in terms of the total weight of the metal elements are as follows. With a coating weight of less than 10 mg/m^2 , the effect of improving the press formability, spot weldability and adhesiveness cannot be obtained. While with a coating weight over 500 mg/m^2 , not only the effect is saturated, but also the formation of the phosphate crystal is inhibited by the presence of the oxide film, thereby deteriorating the chemical treatability.

The reasons why the rate of coating of the Fe-Ni-O film 23 covering the surface of the zinciferous plating layer 22 and having an island-like or mosaic distribution is limited to be within the range of 30 to 90 % per side of the steel sheet are as follows.

If the ratio of coating of the Fe-Ni-O film 23 is less than 30 % per side of the steel sheet, the effect of improving press formability and spot weldability cannot be obtained. While, if the ratio of coating the Fe-Ni-O film 23 exceeds 90% per side of the steel sheet, the area of direct reaction of the phosphate crystal and the zinciferous plated steel sheet is decreased, thereby deteriorating the adhesiveness to the zinciferous plating layer 23.

It is an essential requirement that the Fe-Ni-O film has an island-like or mosaic distribution. The reasons for this are as follows. If the film covers the entire surface of the zinciferous plating layer, when a chemically treated film is formed thereon, the treated film does not react with the zinciferous plating layer, and thus the adhesive force between the chemically treated film and the zinciferous plating layer itself cannot be ensured, thereby deteriorating the adhesive force between the chemically treated film and the zinciferous plating layer itself.

In the Fe-Ni-O film 23, the Fe ratio ($\text{Fe}/(\text{Fe} + \text{Ni})$) of the film is preferably within the range of 0.004 to 0.9. The reasons for this are as follows. With a ratio $\text{Fe}/(\text{Fe} + \text{Ni})$ of less than 0.004, the effect of improving the adhesiveness is low, while with a ratio over 0.9, the effect of improving the spot weldability is low.

The oxygen content of the Fe-Ni-O film is preferably within the range of 0.5 to 10 wt%. The reasons for this are as follows. With an oxygen content of less than 0.5 wt%, since the metallic properties of the film are enhanced, the effect of improving the press formability is low, while with an oxygen content over 10 wt%, the formation of the phosphate crystal is inhibited by the presence of the oxide film, thereby causing the tendency that the chemical treatability deteriorate.

The zinciferous plated steel sheets used in the present invention are steel sheets each having a plating layer formed on a surface of the steel sheet as a base material by a method such as a dip plating method, an electroplating method, a vapor phase plating method or the like. The zinciferous plating layer comprises a single layer or a plurality of layers having a composition containing pure zinc, and a metal or an oxide thereof such as Fe, Ni, Co, Mn, Cr, Al, Mo, Ti, Si, W, Sn, Pb, Nb, Ta, or the like, or at least one organic material. The plating layer may contain fine particles of SiO_2 , Al_2O_3 or the like. A multilayer plated steel sheet and a functional gradient plated steel sheet, in which the composition is changed, can also be used as the zinciferous plated steel sheet.

The method of producing a zinciferous plated steel sheet in accordance with a first manner of the present invention is described. In the first manner, a mist solution having a pH of 1 to 3.5 and containing Fe and Ni ions is sprayed on the surface of the zinciferous plating layer on at least one side of the zinciferous plated steel sheet. After the steel sheet is held at 20 to 70 °C for 1 second or more, it is heated to form, on the surface of the plating layer, the Fe-Ni-O film having an island-like or mosaic distribution, a coating weight of 10 to 1500 mg/m^2 in terms of the total weight of the metallic elements, and a rate of coating of 30 to 90%.

The reason for limiting the pH of the misty solution to be within the range of 1 to 3.5 is that, with a pH beyond this range, no reaction of displacement deposition takes place when the solution adheres to the surface of the zinciferous plated steel sheet, and thus metallic Ni and Fe cannot be formed in the Fe-Ni-O film.

The reason for maintaining the steel sheet at a temperature of 20 to 70 °C for 1 second or more after the mist solution was sprayed thereon is that a time for displacement reaction is ensured for capturing Ni and Fe in the Fe-Ni-O film. The mist solution is preferably a chloride bath having a high efficiency of displacement deposition, and any other solutions such as a sulfate bath, a nitrate bath and the like may be used as long as displacement reaction is secured. In order to improve the efficiency of displacement deposition, additives such as an oxidizer, a surfactant, etc. may be added for facilitating decomposition of the salts during heating.

In order to form the Fe-Ni-O film having a coating weight of 10 to 1500 mg/m² in terms of the total weight of the metal elements, and a rate of coating within the range of 30 to 90 %, the size and amount of the mist particles sprayed or the concentration of the solution may be adjusted.

The reasons why the heating temperature of the zinciferous plated steel sheet on which the mist solution is sprayed is limited to be within the range of 80 to 500 °C are as follows. At a temperature lower than 80 °C, the salts are not decomposed, and thus the Fe-Ni-O film cannot properly be formed, while at a temperature over 500 °C, a problem occurs in which the characteristics of the steel sheet and the plating layer are undesirably changed.

The method of producing a zinciferous plated steel sheet in accordance with a second manner of the present invention is described below. In the second manner, fine irregularities are formed on the surface of the zinciferous plating layer by temper rolling, and treatment for forming a Fe-Ni-O film on the surface of the plating layer on at least one side of the steel sheet is performed for forming the Fe-Ni-O film having an island-like or mosaic distribution, a coating weight of 10 to 1500 mg/m² in terms of the total weight of the metallic elements, and a ratio of coating of 30 to 90%.

Temper rolling of the zinciferous plated steel sheet is performed for correcting the shape and smoothing the surface, and a roll having fine irregularities formed on the surface thereof is used.

Fig. 10 is a schematic drawing illustrating a section of a zinciferous plated steel sheet temper-rolled by using the roll having fine irregularities formed on the surface thereof. As shown in the drawing, fine convex and concave portions 22a and 22b are formed in the surface of a zinciferous plating layer 22 of a steel sheet 21. Treatment for forming a Fe-Ni-O film is then performed on the surface of the zinciferous plated steel sheet on which fine irregularities are formed, to form the Fe-Ni-O film only on the convex portions 22a. As a result, the island-like or mosaic Fe-Ni-O film is formed. This is caused by the fact that the formation reactivity of the Fe-Ni-O film in the convex portions is higher than that in the concave portions. When the Fe-Ni-O film is formed by the electrolysis method, electrolytic current is concentrated at the convex portions. In the aqueous solution dipping method, the convex and concave portions shows different diffusion behaviors of reaction ions in the solution.

A method of producing a zinciferous plated steel sheet in accordance with a third manner is described below. In the third manner, a new surface is formed on the surface of the plating layer by temper-rolling the zinciferous plated steel sheet, and treatment for forming a Fe-Ni-O film is then performed on the surface of the plating layer on at least one side thereof to form the Fe-Ni-O film having an island-like or mosaic distribution, a coating weight of 10 to 1500 mg/m² in terms of the total weight of the metal elements, and a rate of coating of 30 to 90%.

Temper rolling of the zinciferous plated steel sheet is performed for correcting the shape and smoothing the surface, and a rolling roll having a relatively smooth surface thereof is used.

Fig. 11 is a schematic drawing illustrating a section of a zinciferous plated steel sheet temper-rolled by using the rolling roll having a relatively smooth surface. As shown in the drawing, convex portions of fine irregularities originally present on the surface of a zinciferous plating layer 22 of a steel sheet 21 contact the roll to form convex portions 22a where new surfaces appear, and concave portions 22b where no new surface is exposed. Treatment for forming a Fe-Ni-O film is then performed on the surface of the zinciferous plated steel sheet in which the new surfaces appear in the convex portions, to form the Fe-Ni-O film only on the new surfaces of the convex portions 22a. As a result, the island-like or mosaic Fe-Ni-O film is formed. This is caused by the fact that the formation reactivity of the Fe-Ni-O film in the convex portions is higher than that in the concave portions. In the electrolytic method for forming the Fe-Ni-O film, electrolytic current is concentrated at the convex portions, and, in the aqueous solution dipping method, the convex and concave portions shows different diffusion behaviors of reaction ions in the solution, as in the second manner.

A method of producing a zinciferous plated steel sheet in accordance with a fourth manner is described below. In the fourth manner, an air oxide film present on a surface of the plating layer is partly dissolved by dipping the zinciferous plated steel sheet in an acid solution or anodic electrolysis in an acid solution to form active and inactive portions. Treatment for forming a Fe-Ni-O film is then performed to form the Fe-Ni-O film having an island-like or mosaic distribution, a coating weight of 10 to 1500 mg/m² in terms of the total weight of the metal elements, and a ratio of coating of 30 to 90 %.

Fig. 12 is a schematic sectional view of the zinciferous plated steel sheet in which the air oxide coating is partly dissolved by dipping the zinciferous plated steel sheet in an acid solution or anodic electrolysis in an acid solution to form active and inactive portions on the surface of the plating layer. As shown in the drawing, inactive portions 24 where the air oxide film remains and active portions 25 where the air oxide film remains in a thin layer are formed on the surface

of a zinciferous plating layer 22. Treatment for forming a Fe-Ni-O film is then performed on the zinciferous plated steel sheet having the above active and inactive portions to form the Fe-Ni-O film 23 only on the active portions. As a result, the island-like or mosaic Fe-Ni-O film is formed. This is caused by the fact that the Fe-Ni-O film in the active portions has higher formation reactivity. In the electrolytic method for forming the Fe-Ni-O film, electrolytic current is concentrated at the active portions, and, in the aqueous solution dipping method, the active portions have high activity.

A method of producing a zinciferous plated steel sheet in accordance with a fifth manner is described below. In the fifth manner, an alkaline solution is used in place of the acid solution used in the fourth manner, and the same effects are obtained. Namely, an air oxide film present on a surface of the plating layer is partly dissolved by dipping the zinciferous plated steel sheet in an alkaline solution or anodic electrolysis in an alkaline solution to form active and inactive portions. Treatment for forming a Fe-Ni-O film is then performed to form the Fe-Ni-O film having an island-like or mosaic distribution, a coating weight of 10 to 1500 mg/m² in terms of the total weight of the metal elements, and a rate of coating of 30 to 90%.

When an air oxide film present on a surface of the plating layer is partly dissolved by dipping the zinciferous plated steel sheet in the alkaline solution or by anodic electrolysis in the alkaline solution to form the active and inactive portions, the steel sheet has the same sectional state as that shown in Fig. 12. Treatment for forming the Fe-Ni-O film is then performed on the zinciferous plated steel sheet to form the Fe-Ni-O film only on the active portions. As a result, the island-like or mosaic Fe-Ni-O film is formed. This is caused by the fact that the Fe-Ni-O film in the active portions has higher formation reactivity. In the electrolytic method for forming the Fe-Ni-O film, electrolytic current is concentrated at the active portions, and, in the aqueous solution dipping method, the active portions have high activity, as in the fourth manner.

In the treatment for the Fe-Ni-O film, the Fe-Ni-O film can be formed by cathodic electrolysis using an electrolytic solution having a pH of 1 to 2 and containing nickel sulfate, ferrous sulfate and ferric sulfate in a total amount of 0.3 to 2.0 mol/l.

It is also preferable that the ratio of the Fe content (g/l) to the total of the Fe content (g/l) and the Ni content (g/l) in the electrolytic solution is controlled to be within the range of 0.004 to 0.9, and the molar ratio of ferrous sulfate (mol/l) to the total of the ferrous sulfate (mol/l) and ferric sulfate (mol/l) is controlled to be within the range of 0.5 to less than 1.0. The reasons why these conditions are preferable are as follows. If the Fe ratio (Fe/(Fe+Ni)) of the electrolytic solution is less than 0.004, the Fe content of the Fe-Ni-O film is decreased, and the effect of improving adhesiveness is thus decreased. While if the Fe ratio exceeds 0.9, the Fe content of the Fe-Ni-O film is increased, and the effect of improving the spot weldability is thus decreased. With a molar ratio of ferric sulfate (ferric sulfate/ferrous sulfate + ferric sulfate) of less than 0.5, the oxygen content of the Fe-Ni-O film is decreased. On the other hand, the higher the molar ratio is, the more easily the iron oxide is captured in the Fe-Ni-O film, and the higher the oxygen content becomes. However, the electrolytic solution containing only ferric sulfate is undesirable because yellowing occurs in plating.

In the treatment for forming the Fe-Ni-O film, the Fe-Ni-O film is preferably formed by treatment with an aqueous solution containing FeCl₂ and NiCl₂ at a pH of 2.0 to 3.5 and a temperature of 20 to 70 °C. The ratio of Fe content (g/l) to the total of the Fe content (g/l) and the Ni content (g/l) is further preferably controlled to 0.004 to 0.9.

Examples

Examples within the range of the present invention and comparative examples out of the range of the present invention were carried out as described below.

As the zinciferous plated steel sheets used in the examples and comparative examples, the seven types of steel sheets below respectively denoted by symbols A to G were appropriately selected according to the plating methods, the compositions and the coating weights.

A: Alloyed zinc dip-plated steel sheet (10 wt% Fe, the balance Zn) both sides of which had a coating weight of 60 g/m².

B: Zinc dip-plated steel sheet both sides of which had a coating weight of 90 g/m².

C: Zinc electroplated steel sheet both sides of which had a coating weight of 40 g/m².

D: Zn-Fe alloy electroplated steel sheet (15 wt% Fe) both sides of which had a coating weight of 40 g/m².

E: Zn-Ni alloy electroplated steel sheet (12 wt% Ni) both sides of which had a coating weight of 30 g/m².

F: Zn-Cr alloy electroplated steel sheet (4 wt% Cr) both sides of which had a coating weight of 20 g/m².

G: Zn-Fe alloy dip-plated steel sheet (5 wt% Al) both sides of which had a coating weight of 60 g/m².

In the examples of the present invention, the Fe-Ni-O film having an island-like or mosaic distribution was formed on the plating layer of each of the above types of zinciferous plated steel sheets by the following methods I) to V):

I) On the basis of the first manner of the present invention, a zinciferous plated steel sheet was produced in which a Fe-Ni-O film had an island-like or mosaic distribution.

The mist solution containing Fe and Ni ions was sprayed on the zinciferous plated steel sheet, and the steel sheet was then heated to form the film. The other main conditions were as follows:

Components of the solution: nickel chloride and iron chloride
 Metal ion content of the solution: 1 to 10 g/l
 Amount of the solution sprayed: controlled to obtain a predetermined coating weight
 Holding time after spraying the solution: 1 to 30 seconds
 Heating temperature: 200 to 350 °C
 Heating time: 1 minute

II) On the basis of the second manner of the present invention, a zinciferous plated steel sheet was produced in which a Fe-Ni-O film had an island-like or mosaic distribution.

Fine irregularities (irregularity pitch: 50 to 300 μm) were formed on the zinciferous plating layer surface by temper-rolling the zinciferous plated steel sheet, and treatment for forming the Fe-Ni-O film was then performed by the cathodic electrolysis method 1 or aqueous solution dipping method 2 below.

1. Cathodic electrolysis method

Electrolytic solution: Solution containing nickel sulfate, ferrous sulfate and ferric sulfate
 Electrolytic solution concentration: 0.3 to 2.0 mol/l (total concentration of components)
 pH: 1 to 2
 Fe ratio in the electrolytic solution (Fe/(Fe+Ni)): 0.004 to 0.9
 Molar ratio of ferric sulfate of the electrolytic solution
 (ferric sulfate/ferrous sulfate+ferric sulfate): 0.5 to 1.0

2. Aqueous solution dipping method

Aqueous solution and component content:
 nickel chloride = 120 g/l
 ferrous chloride = changing concentrations
 pH: 2.5 to 3.5
 Fe ratio of the aqueous solution (Fe/(Fe+Ni)): 0.004 to 0.9
 Dipping time: 1 to 30 seconds

III) On the basis of the third manner of the present invention, a zinciferous plated steel sheet was produced in which a Fe-Ni-O film had an island-like or mosaic distribution.

A new surface (pitch of new surface: 10 to 50 μm) was formed on the zinciferous plating layer by temper-rolling the zinciferous plated steel sheet, and treatment for forming the Fe-Ni-O film was then performed.

The film was formed by the aqueous solution dipping method 2 described above in II).

IV) On the basis of the fourth manner of the present invention, a zinciferous plated steel sheet was produced in which a Fe-Ni-O film had an island-like or mosaic distribution.

The air oxide film present on the surface of the zinciferous plating layer was partly dissolved by dipping the zinciferous plated steel sheet in a sulfuric acid solution of pH 3 for 2 to 5 seconds to form active and inactive portions on the surface of the plating layer, and treatment for forming the Fe-Ni-O film was then performed.

The film was formed by either of the cathodic electrolysis method 1 and the aqueous solution dipping method 2.

V) On the basis of the fifth manner, a zinciferous plated steel sheet was produced in which a Fe-Ni-O film had an island-like or mosaic distribution.

The air oxide film present on the surface of the zinciferous plating layer was partly dissolved by dipping the zinciferous plated steel sheet in a NaOH alkaline solution of pH 12 for 2 to 5 seconds to form active and inactive portions on the surface of the plating layer, and treatment for forming the Fe-Ni-O film was then performed.

The film was formed by either of the cathodic electrolysis method 1 and the aqueous solution dipping method 2.

On the other hand, in the comparative examples, a zinciferous plated steel sheet was prepared by a method in which the Fe-Ni-O film was formed under conditions beyond the range of the present invention, or no treatment was formed for forming the film.

Tables 22 to 26 show the plating layer type (denoted by a symbol) and the coating weight of the zinciferous plating layer, the method (denoted by a symbol) of forming the Fe-Ni-O film, and the coating weight thereof in terms of the total

weight of metal elements and the rate of coating of each of the examples and the comparative examples.. Tables 25 and 26 further show the Fe ratio ($\text{Fe}/(\text{Fe}+\text{Ni})$) of the film and the oxygen content thereof of each of the examples and the comparative examples.

Table 22

	Lower Layer		Fe-Ni-O Film			Press-Formability Friction Coefficient	Spot Weldability Number of Continuous Welding Spots	Chemical Treatability	Adhesion Between Treated Film and Zinc Layer
	Type	Coating Weight (g/m ²)	Forming Method	Coating Weight (mg/m ²)	Rate of Coating (%)				
1	Comparative Example	A	60	-	-	0	0.165	3000	Δ
2	Example	A	60	I	-	200	0.145	5000 points or more	0
3	Example	A	60	I	-	200	0.135	5000 points or more	0
4	Example	A	60	I	-	200	0.125	5000 points or more	0
5	Example	A	60	II	1	200	0.140	5000 points or more	0
6	Example	A	60	II	1	200	0.130	5000 points or more	0
7	Example	A	60	II	2	200	0.140	5000 points or more	0
8	Example	A	60	II	2	200	0.130	5000 points or more	0
9	Comparative Example	A	60	III	2	5	0.155	4000	Δ
10	Example	A	60	III	2	10	0.140	5000 points or more	0
11	Example	A	60	III	2	50	0.135	5000 points or more	0
12	Example	A	60	III	2	100	0.132	5000 points or more	0
13	Comparative Example	A	60	III	2	200	0.155	5000 points or more	0
14	Example	A	60	III	2	200	0.142	5000 points or more	0
15	Example	A	60	III	2	200	0.132	5000 points or more	0
16	Example	A	60	III	2	200	0.125	5000 points or more	0
17	Comparative Example	A	60	III	2	200	0.125	5000 points or more	Δ
18	Example	A	60	III	2	400	0.120	5000 points or more	0

Table 23

	Lower Layer		Fe-Ni-O Film			Press- Moldability Friction Coefficient	Spot Weldability Number of Continuous Welding Spots	Chemical Treatability	Adhesion Between Treated Film and Zinc Layer
	Type	Coating Weight (g/m ²)	Forming Method	Coating Weight (mg/m ²)	Rate of Coating (%)				
19 Example	A	60	III	2	700	70	0.120	5000 points or more	0
20 Example	A	60	III	2	1000	70	0.115	5000 points or more	0
21 Example	A	60	III	2	1500	70	0.115	5000 points or more	0
22 Comparative Example	A	60	III	2	1600	70	0.115	5000 points or more	0
23 Example	A	60	IV	1	200	40	0.140	5000 points or more	0
24 Example	A	60	IV	1	200	70	0.130	5000 points or more	0
25 Example	A	60	IV	2	200	40	0.140	5000 points or more	0
26 Example	A	60	IV	2	200	70	0.130	5000 points or more	0
27 Example	A	60	V	1	200	40	0.140	5000 points or more	0
28 Example	A	60	V	2	200	70	0.130	5000 points or more	0
29 Example	A	60	V	2	200	40	0.140	5000 points or more	0
30 Example	A	60	V	2	200	70	0.130	5000 points or more	0
31 Comparative Example	B	90	-	-	0	0	0.180	2000	Δ
32 Example	B	90	III	2	200	30	0.145	5000 points or more	0
33 Example	B	90	III	2	200	70	0.135	5000 points or more	0
34 Comparative Example	C	40	-	-	0	0	0.165	4000	Δ
35 Example	C	40	III	2	200	30	0.135	5000 points or more	0
36 Example	C	40	III	2	200	70	0.125	5000 points or more	0

Table 24

	Lower Layer		Fe-Ni-O Film			Press- Moldability Friction Coefficient	Spot Weldability Number of Continuous Welding Spots	Chemical Treatability	Adhesion Between Treated Film and Zinc Layer
	Type	Coating Weight (g/m ²)	Forming Method	Coating Weight (mg/m ²)	Rate of Coating (%)				
37	Comparative Example	40	-	0	0	0.165	4000	Δ	0
38	Example	40	III	200	30	0.135	5000 points or more	0	0
39	Example	40	III	200	70	0.125	5000 points or more	0	0
40	Comparative Example	30	-	0	0	0.165	4000	Δ	0
41	Example	30	III	200	30	0.135	5000 points or more	0	0
42	Example	30	III	200	70	0.125	5000 points or more	0	0
43	Comparative Example	20	-	0	0	0.165	4000	Δ	0
44	Example	20	III	200	30	0.135	5000 points or more	0	0
45	Example	20	III	200	70	0.125	5000 points or more	0	0
46	Comparative Example	60	-	0	0	0.180	2000	Δ	0
47	Example	60	III	200	30	0.145	5000 points or more	0	0
48	Example	60	III	200	70	0.135	5000 points or more	0	0

Table 25

	Lower Layer		Fe-Ni-O Film				Press- Formability Friction Coefficient	Spot Weldability Number of Continuous Welding Spots	Adhesion Peel Strength (kgf/25mm)	Chemical Treatability
	Type	Coating Weight (g/m ²)	Forming Method	Coating Weight (mg/m ²)	Rate of Coating (%)	Fe/ (Fe-Ni)	Oxygen Content (%)			
49	Comparative Example	A	-	-	-	-	-	3000	8.0	Δ
50	Comparative Example	A	III	200	70	0	3	8000	7.0	0
51	Example	A	III	200	70	0.003	3	8000	8.0	0
52	Example	A	III	200	70	0.004	3	8000	11.0	0
53	Example	A	III	200	70	0.010	3	8000	11.5	0
54	Example	A	III	200	70	0.050	3	8000	12.0	0
55	Example	A	III	200	70	0.100	3	8000	12.5	0
56	Example	A	III	200	70	0.150	3	8000	12.5	0
57	Example	A	III	200	70	0.200	3	8000	12.5	0
58	Example	A	III	200	70	0.250	3	8000	12.5	0
59	Example	A	III	200	70	0.300	3	8000	12.5	0
60	Example	A	III	200	70	0.500	3	7000	12.5	0
61	Example	A	III	200	70	0.700	3	6000	12.5	0
62	Example	A	III	200	70	0.900	3	5000	12.5	0
63	Example	A	III	200	70	0.920	3	4000	12.5	0
64	Comparative Example	A	III	200	70	1	3	3000	12.5	0

Table 26

	Lower Layer		Fe-Ni-O Film				Press-Formability	Spot	Adhesion	Chemical Treatability
	Type	Coating Weight (g/m ²)	Forming Method	Coating Weight (mg/m ²)	Rate of Coating (%)	Fe/(Fe+Ni)	Oxygen Content (%)			
65	Comparative Example	A	60	III	2	200	70	0.2	0	0
66	Example	A	60	III	2	200	70	0.2	0.4	0
67	Example	A	60	III	2	200	70	0.2	0.5	0
68	Example	A	60	III	2	200	70	0.2	1	0
69	Example	A	60	III	2	200	70	0.2	5	0
70	Example	A	60	III	2	200	70	0.2	7	0
71	Example	A	60	III	2	200	70	0.2	10	0
72	Example	A	60	III	2	200	70	0.2	11	Δ

The coating weight, the ratio of coating, the Fe ratio and the oxygen content of the Fe-Ni-O film were measured by the following methods.

[Measurement of the coating weight and the ratio Fe/(Fe+Ni) of the film]

In specimens of the dip-plated steel, electroplated steel, Zn-Cr alloy electroplated steel, and Zn-Al alloy dip-plated steel, which are denoted by symbols B, C, F and G, respectively, the Fe-Ni-O film was peeled together with the surface layer of the lower plating layer (representing the Zn-based plating layer hereinafter) by dissolving in diluted hydrochloric acid, and the coating weight and composition of the Fe-Ni-O film were measured by ICP quantitative analysis of Fe, Ni and metals. The ratio Fe/(Fe + Ni) of the film was calculated.

In specimens of the alloyed zinc dip-plating steel, Zn-Fe alloy electroplated steel, and Zn-Ni alloy electroplated steel, which are denoted by symbols A, D, and E, respectively, since the lower plating layer contained the same component elements as those in the Fe-Ni-O film, the component elements of the upper Fe-Ni-O film could not be easily completely separated from the component elements of the lower plating layer by the ICP method, only the elements of the Fe-Ni-O film, which are not contained in the lower plating layer, were thus quantitatively analyzed by the ICP method. After Ar ion sputtering, the component elements of the Fe-Ni-O film was then repeatedly measured from the surface by the XPS method to measure the composition distribution of each of the component elements in the direction of the depth of the plating layer. In this measurement, the distance between the surface and the center between a depth where the element of the Fe-Ni-O film, which was not contained in the lower plating layer, showed the maximum content, and a depth where that element was not detected, was considered as the thickness of the Fe-Ni-O film. The coating weight and the composition of the Fe-Ni-O film were calculated from the results of the ICP method and the XPS method. The ratio Fe/(Fe + Ni) of the film was then calculated.

[Measurement of ratio of coating]

The ratio of coating of the Fe-Ni-O film distributed in an island-like and mosaic form was measured by the following method.

Mapping analysis of the surface having the Fe-Ni-O film formed thereon was performed by an AES analysis (Auger electron spectroscopy) or EPMA analysis to measure distribution states of Ni, Fe and O on the surface. Points exhibiting an intensity showing a coating weight of the Fe-Ni-O film of 10 mg/m² or more in terms of the total weight of the metal elements was considered as coated points, and the ratio of coating was calculated by determining the ratio of the coated points to the total measurement points.

[Measurement of oxygen content of film]

The oxygen content of the film was determined from the results of AES analysis in the direction of the depth thereof.

Specimens (Nos. 1 to 72) of the examples and the comparative examples were evaluated in the press formability, the spot weldability and chemical treatability, specimen Nos. 1 to 48 were further evaluated in the adhesiveness between the chemically treated film and the zinciferous plating layer itself, and specimen Nos. 49 to 72 were further evaluated in adhesion to an adhesive.

[Adhesion test of conversion-treated film]

A specimen was treated with a dip-type zinc phosphate treating agent for undercoating an automobile, followed by ED coating with a thickness of 20 μm.

As shown in Fig. 13, two specimens 35 having a the size of 100 x 25 mm were bonded with an adhesive agent 37 having a thickness of 0.15 and a bonding area of 25 x 10 mm, and spacers 16 of 0.15 mm therebetween to prepare a test specimen, followed by baking at 170 °C for 30 minutes. An epoxy adhesive agent for structures was used as the adhesive agent. Although various steel sheets having a thickness of 0.8 mm were used as specimens, since some materials have the possibility of causing breakage of a base material due to low strength during a tensile test, a steel sheet having a thickness of 2 mm was used as an reinforcing plate 39 for a specimen to form a test specimen. Thus-formed test specimen was pulled at a ratio of 200 mm/min by using a tensile machine to measure the average peeloff strength at the time of peeling, and the peeled surface was observed by a scanning electron microscope (SEM).

Peeling occurs at a position with lowest strength. In the use of GA (symbol A), peeling occurs at the interface between the GA deposit and the steel sheet, and peeloff strength represents the interface peeloff strength between the GA film and the steel sheet. In the use of each of GI (symbol B), EG (symbol C), Zn-Fe (symbol D), Zn-Ni (symbol E), Zn-Cr (symbol F) and Zn-Al (symbol G), aggregation in the adhesive is broken, and thus peeloff strength represents the strength of the adhesive itself.

If the film of the present invention covers the entire zinciferous plating layer, the adhesion between the chemically treated film and the zinciferous plating layer itself is not ensured, thereby decreasing the peeloff strength. The peeloff strength in the same level as an untreated specimen is shown by ○, and the peeloff strength lower than the untreated specimen is shown by X.

The test results of each of the test specimens measured by the above described measurements are shown in Tables 22 to 26. These tables reveal the following results.

The examples within the range of the present invention have low friction coefficients and good press formability. Particularly, in the present invention, since the Fe-Ni-O film has an island-like or mosaic distribution, if the coating weight and other conditions are considered as the same, as the ratio of coating on the surface of the plating layer increases, the friction coefficient decreases, and thus the film more contributes to improvement in the press formability.

In all the examples, the results of continuous spot welding test for the spot weldability are 5000 spots or more and are thus very good.

In the examples, the crystal of the zinc phosphate coating is normally formed, and thus the chemical treatability are good.

In regard to the adhesion between the chemically treated film and the zinciferous plating layer, when the Fe-Ni-O film covers the entire zinciferous plating layer, the adhesive force between the chemically treated film and the zinciferous plating layer is not secured, thereby decreasing peeloff strength. In Comparative Example No. 17 in which the rate of coating by the Fe-Ni-O film is 100%, the adhesion is not secured. However, in all examples, the adhesion is secured.

In most of the examples, the peeloff strength is 12 kgf/25 mm or more and thus good.

The comparative examples beyond the range of the present invention are poor in any one of the friction coefficient, the continuous spot weldability, adhesiveness and the chemical treatability.

In the present invention constructed as described above, since the Fe-Ni-O film formed on the surface of the plating layer a zinciferous plated steel sheet has improved performance, higher hardness and melting point than those of a zinc or zinc alloy plating layer, and an island-like or mosaic distribution, in press forming, the sliding resistance between the surface of the plating layer and a press die is significantly decreased, and the zinciferous plated steel sheet can easily be flowed into the press die, thereby improving the press formability. The continuous spot weldability in spot welding are also improved due to the presence of the Fe-Ni-O film having a high melting point. The presence of the Fe oxide in the Fe-Ni-O film further increases the peeloff strength of an adhesive plate and thus improves adhesiveness. The chemical treatability are also more improved due to the above characteristics as well as the island-like or mosaic distribution of the film. The present invention thus has the very advantageous industrial effect of providing a zinciferous plated steel sheet having excellent press formability, spot weldability, adhesiveness and chemical treatability.

EMBODIMENT 6

First, a method for producing a zinciferous plated steel sheet is characterized in that the zinciferous plated steel sheet is subjected to temper rolling within the range of elongation rate of 0.3 to 5.0 %, alkali treatment is carried out for the zinciferous plated steel sheet in an alkaline solution having pH of 10 or more for the period of 2 to 30 seconds, and subsequently a Fe-Ni-O film is formed on the surface of a plating layer of the zinciferous plated steel sheet for which the alkali treatment is carried out.

Secondly, a method for producing a zinciferous plated steel sheet is characterized in that alkali treatment is carried out for the zinciferous plated steel sheet in an aqueous solution having pH of 10 or more within the period of 2 to 30 seconds, the zinciferous plated steel sheet for which alkali treatment is carried out in that way is subjected to temper rolling within the range of 0.3 to 5.0 %, and subsequently, a Fe-Ni-O film is formed on the surface of a plating layer of the zinciferous plated steel sheet thus subjected to the temper rolling.

A method for forming the Fe-Ni-O film can be performed by treating the zinciferous plated steel sheet in an aqueous solution having the range of pH of 2.0 to 3.5 at a temperature of 20 to 70 °C, the aqueous solution containing FeCl₂ and NiCl₂.

The formation of the Fe-Ni-O film is conducted by treating the zinciferous plated steel sheet in an aqueous solution having of pH of 2.0 to 3.5 at a temperature of 20 to 70 °C, the aqueous solution containing FeCl₂ and NiCl₂ and a content ratio of a sum of Fe content (wt. %) and Ni content (wt. %) to the Fe content (wt. %) being within the range of 0.004 to 0.9.

In this patent application, it is to be noted that in the case that a Fe-Ni-O film formed on the surface of the plating layer of the zinciferous plated steel sheet to serve as an upper layer is referred to, it is called "film", and in the case that a zinciferous plating layer serving as a lower layer is referred to, it is called "plating layer" but it is not called "film".

The reasons why production conditions of the invention are defined as mentioned above are described below.

In the invention, the reason why the zinciferous plated steel sheet is treated in the alkaline solution having pH of 10 or more for the period of 2 to 30 seconds and thereafter the Fe-Ni-O film is formed on the surface of the zinciferous plated steel sheet consists in that the case that the zinciferous plated steel sheet is treated in the alkaline solution is remarkably superior in press formability in comparison with the case that the Fe-Ni-O film is formed without any treatment of the zinciferous plated steel sheet in the alkaline solution. In addition, the foregoing reason consists in that the zinciferous plated steel sheet having adhesiveness improved and exhibiting excellent press formability can be obtained, because when the Fe-Ni-O film is formed after it is subjected to temper rolling within the range of elongation ratio of 0.3 % to 0.5 % before or after it is treated in the alkaline solution, the surface of the zinciferous plated steel sheet is flattened

by the temper rolling and the oxide film worsening the adhesiveness of the Fe-Ni-O film is removed.

Fig. 14 is a graph which shows the relationship between a coating weight of Ni to the surface of the plating layer of the zinciferous plated steel sheet with respect to the case that alkaline solution treatment and temper rolling are conducted as well as the case that no treatment is conducted. It is found from the graph that in the case that alkaline solution treatment and temper rolling are conducted, a value of frictional coefficient becomes small with a same coating weight of nickel compared with the case that no treatment is conducted. Here, the aqueous solution containing one kind or two and more kinds of alkaline chemicals such as NaOH, KOH, Na_2SO_4 , LiOH, Na_2SO_4 , MgOH or the like can be used as an alkaline solution. It is necessary that an alkali concentration of the aqueous solution has pH of 10 or more and it is more desirous that the alkaline solution is prepared so that the alkaline concentration has pH of 11 and more. In this case, it is generally acceptable that the alkaline solution has a concentration ranging from 5 to 50 g/l.

On the contrary, in the case that the Fe-Ni-O film is formed after the zinciferous plated steel sheet is treated in an acid solution, some improvement of press formability is recognized but press formability, spot weldability and adhesiveness are inferior compared with the case that the zinc based sheets steel sheet is treated in the alkaline solution. This is attributable to the fact that the adhesiveness of the Fe-Ni-O film are improved by treating the zinciferous plated steel sheet in the alkaline solution, and it is appreciated that the foregoing effect can not be obtained when the zinciferous plated steel sheet is treated in the acid solution because a quantity of oxide film unavoidably formed on the surface of the zinciferous plated steel sheet is increased with the acid solution.

Here, the Fe-Ni-O film is a mixture of Fe metal, Fe oxide, Ni metal and Ni oxide, and a method of forming the film is not especially defined to certain one. It is acceptable that it is treated in an aqueous solution containing Fe ion, Ni ion and an oxidizing agent, and an aqueous solution dipping method, an aqueous solution spraying method, a coating method, an electroplating method or the like are employable. In addition, a vapor phase plating method such as a laser CVD, an optical CVD, a vacuum deposition, a sputtering deposition or the like can be employed.

A plus ion, hydroxide and oxide of Zn, Co, Mn, Mo, Al, Ti, Sn, W, Si, Pb, Nb, Ta or the like unavoidably contained in the plating layer for the zinciferous plated steel sheet used for carrying out the present invention are contained in the aqueous solution for forming the film. In addition, a minus ion may be contained in the plating layer.

Additionally, to elevate the properties of alkali treatment for the zinciferous plated steel sheet, a surface active agent may additionally be contained in the alkaline solution. However, when an oxidizing agent is added to the alkaline solution, an oxide is formed on the surface of the zinciferous plated steel sheet, causing the adhesiveness of the Fe-Ni-O film to be degraded. For this reason, it is not desirable that the surface active agent is additionally contained in that way.

Temper rolling and alkali treatment can be conducted regardless of an order of both the treatments before Fe-Ni-O film forming treatment with same effect, provided that a factor of obstructing a coating weight of the Fe-Ni-O film is removed. Therefore, the foregoing order of both the treatments for removing the obstructing factor may adequately selected depending on the kind of the zinciferous plated steel sheet. With respect to the elongation ratio for the temper rolling, it is sufficient that the factor for obstructing the adhesiveness of Fe-Ni-O film is removed. To this end, it is acceptable that the elongation ratio ranges from 0.3 % to 5.0 %. When same elongation ratio is applied, a larger compression load provides a larger effect with the same elongation ratio. When the elongation ratio is less than 0.3 %, the flattening effect is small, resulting in the satisfactory press formability failing to be obtained. On the other hand, when the elongation ratio exceeds 5.0 %, the material is undesirably degraded.

The reason why the aqueous solution containing FeCl_2 and NiCl_2 therein used for forming the Fe-Ni-O film with the method consists in that a high precipitation efficiency is obtained when metal salt of chloride is used to provide secondary iron ion and nickel ion, resulting in productivity of the method being improved. In the case of same salt concentration and same treatment time, a coating weight of Ni and Fe is increased in comparison with that of nitrate and sulfate.

Fig. 15 is a graph which shows the relationship between the kind of treatment bath for forming the Fe-Ni-O film and a coating weight. The graph shows the case that a concentration ratio of Ni to Fe in the treatment bath is 90 : 10 and a sum of concentrations in the stationary bath is 100 g/l. It is found from the graph that a chloride bath exhibits a high efficiency compared with a sulfate bath and a nitride bath.

It is desirable that pH of the aqueous solution for forming the film ranges from 2.0 to 3.5. The reasons for this are described below.

When pH is less than 2.0, a quantity of generation of hydrogen from the cathode is excessively increased, a precipitation efficiency is lowered and a coating weight of Ni and Fe becomes small with same salt concentration and same treatment time, resulting in productivity of the method being lowered. In addition, the film is mainly composed of metals of Ni and Fe, and improvement effect of press formability, spot weldability and adhesiveness can not be achieved. On the other hand, when pH exceeds 3.5, Fe in the aqueous solution is intensely oxidized, and flaw on the surface of the steel sheet appears in the presence of sludge.

Fig. 16 is a graph which shows by way of example a coating weight of Ni to the dipping time in the case that pH is changed from 2.0 to 3.5. The graph shows the case that the treatment bath has a temperature of 50 °C, the concentration ratio of Ni to Fe in the treatment bath is 20 : 80, and a sum of concentrations is 100 g/l, and it is found from the graph that the precipitation efficiency is acceptable as pH is increased.

It is desirable that the temperature of the aqueous solution for forming the film ranges from 20 °C to 70 °C. The rea-

sons for this are described as follows.

When the temperature of the aqueous solution is lower than 20 °C, the reaction speed becomes slow and a long time is required to maintain a coating weight of Ni and Fe necessary for improving the properties of the film. On the other hand, when the temperature of the aqueous exceeds 70 °C, deterioration of the properties of the aqueous solution is accelerated and facilities and thermal energy for maintaining them at a high temperature are required, resulting in the production cost being elevated.

The reason why a ratio of a sum of Fe content (wt. %) and Ni content (wt. %) to the Fe content (wt. %) in an aqueous solution serving as a solution for forming Fe-Ni-O film (hereinafter represented by Fe ratio : $\text{Fe}/(\text{Fe} + \text{Ni})$) is defined within the range of 0.004 to 0.9 consists in that when the Fe ratio is less than 0.004, the adhesiveness can not be improved and when it exceeds 0.9, the properties of spot weldability can be improved to small extent.

A steel sheet having a zinciferous plating layer formed thereon by employing a zinc dip-plating method, an electroplating method, a vapor plating method or the like is acceptable as a zinciferous plated steel sheet which can be used for carrying out the present invention. The composition of the plating layer on the surface of the zinciferous plated steel sheet may be composed of a metal such as Fe, Ni, Co, Mn, Cr, Al, Mo, Ti, Si, W, Sn, Pb, Nb and Ta (in this case, Si is handled as metal) in addition to pure zinc or oxide or one kind or two and more kinds of organic material in the form of plating layer of single or plural layers. In addition, fine particles of SiO_2 and Al_2O_3 may be contained in the plating layer. Further, a plural layer plated steel sheet having a composition of a plating layer changed and a function inclined plated steel sheet can be used as a zinciferous plated steel sheet.

A phenomenon of adhesion between the steel sheet and the forming die at the time of press forming disappears in the presence of Fe-Ni-O film formed on the surface of the plating layer of the zinciferous plated steel sheet under the foregoing limiting conditions, causing slidable resistance to be reduced. Thus, sliding receipt of the steel sheet in the forming die is improved and formation of brittle alloy layer between copper electrodes at the time of spot welding is suppressed with the result that continuous spot-weldability are improved, and moreover, adhesiveness are improved by the function of the film containing Fe therein.

Examples

Predetermined zinciferous plated steel sheets were produced on the basis of the examples which represent the method defined within the scope of the present invention as well as the comparative examples which represent the method defined outside of the scope of the present invention, using zinciferous plated steel sheets which are plated on cold rolled thin steel sheets by employing conventional method. The kind of plating of the zinciferous plated steel sheet was selected from the group represented by the following characters A, B, C, D, E, F and G.

A: Alloyed zinc dip-plating layers of alloy composed of 10 wt. % Fe and balance of Zn are formed and a coating weight of the alloy to both of the surfaces is defined to 60 g/m².

B: Zinc dip-plating layers are formed and a coating weight to both of the surfaces is defined to 90 g/m².

C: Zinc Electroplating layers are formed and a coating weight of the alloy to both of the surfaces is defined to 40 g/m².

D: Zinc Electroplating layers of 15 wt. % of Fe and balance of Zn are formed and a coating weight of the alloy to both of the surfaces is defined to 40 g/m².

E: Alloy Electroplating layers of 12 wt. % Ni and balance of Zn are formed and a coating weight of the alloy to both of the surfaces is defined to 30 g/m².

F: Alloy Electroplating layers of 4 wt. % Cr and balance of Zn are formed and a coating weight of the alloy to both of the surfaces is defined to 20 g/m².

G: Alloy dip-plating layer of 5 wt. % Al and balance of Zn are formed and a coating weight of the alloy to both of the surfaces is defined to 60 g/m².

The zinciferous plated steel sheets produced by employing the methods of examples and comparative examples were evaluated during the following tests 1 and 2 with respect to press formability, spot weldability, adhesiveness, chemical treatability and mechanical properties of the zinciferous plated steel sheet.

Next, examples and comparative example are described with respect to tables 1 to 3. An outline of the content of each test is shown in Table 27.

Table 27

Temper Rolling				Alkali Treatment				Formation of Fe-Ni-O				Film																	
Kind of Plating	Elongation Rate (%)	Time of Execution of Treatment Before or After Alkali Treatment	Solution Component	pH	Method of Treatment	Temperature (°C)	Time (s)	Presence or Absence of Film	Method of Formation	Aqueous Solution																			
										FeCl ₂ + NiCl ₂ (wt.%)	pH	Temperature	Treatment Time	Fe															
Test 1	A	0.7	Before and After	NaOH	9.5-14.0	Dipping	50	5	Presence	Dipping	-	-	-	-	-														
																1 of Test 1	A	0.2-5.5	Before and After	NaOH	12.0	Dipping	50	5	Presence	Dipping	-	-	-
																2 of Test 1													
3 of Test 1	A	0.7	Before	Various Kind	12.0 & 2.0	Dipping and spraying	50	5	Presence	Dipping and Various Kind	-	-	-	-	-														
Test 2	B-G	0 & 0.7	Before	NaOH	12.0		50	5	Presence	Dipping	-	-	-	-	-														
Test 3	A	0.7	Before and After	NaOH	12.0		50	5	Presence	Dipping	200	2.5	50	5	0-1														

[Test 1]

(1 OF TEST 1)

5 As shown in Table 28 representing test conditions, zinciferous plated steel sheets of which kind of plating is identified by marks A are subjected to constant temper rolling at an elongation ratio of 0.7 % before or after alkali treatment, they are subjected to preliminary treatment by dipping them in an aqueous solution of NaOH having pH ranging from 9.5 to 14.0 at a temperature of 50 °C, and subsequently, on completion of the preliminary treatment, Fe-Ni-O film is formed on the surface of each zinciferous plated steel sheet by dipping it in an aqueous solution containing FeCl₂ and NiCl₂. In addition, the case that alkali treatment is not conducted and Fe-Ni-O film is not formed, the case that preliminary treatment is conducted but Fe-Ni-O film is not formed and the case that Fe-Ni-O film is formed without any alkali treatment conducted are shown as comparative examples.

Table 28

No.	Kind of Plating	Conditions for Temper Rolling		Conditions for Alkali Treatment					Fe-Ni-O film		Test Sample
		Elongation Rate %	Before or After Alkali Treatment	Solution		Method of Treatment	Temperature (°C)	Time (s)	Presence or Absence of Film	Method of Film Formation	
				Component	pH						
1	A	0.7	-	-	-	-	-	-	X	-	Comparative Example
2	A	0.7	Before	NaOH	12.0	Dipping	50	5	X	-	Comparative Example
3	A	0.7	-	-	-	-	-	-	O	Dipping	Comparative Example
4	A	0.7	Before	NaOH	9.5	Dipping	50	5	O	Dipping	Comparative Example
5	A	0.7	Before	NaOH	10.5	Dipping	50	5	O	Dipping	Embodiment Example
6	A	0.7	After	NaOH	10.5	Dipping	50	5	O	Dipping	Embodiment Example
7	A	0.7	Before	NaOH	11.0	Dipping	50	5	O	Dipping	Embodiment Example
8	A	0.7	After	NaOH	11.0	Dipping	50	5	O	Dipping	Embodiment Example
9	A	0.7	Before	NaOH	11.5	Dipping	50	5	O	Dipping	Embodiment Example
10	A	0.7	After	NaOH	11.5	Dipping	50	5	O	Dipping	Embodiment Example
11	A	0.7	Before	NaOH	13.0	Dipping	50	5	O	Dipping	Embodiment Example
12	A	0.7	After	NaOH	13.0	Dipping	50	5	O	Dipping	Embodiment Example
13	A	0.7	Before	NaOH	14.0	Dipping	50	5	O	Dipping	Embodiment Example
14	A	0.7	After	NaOH	14.0	Dipping	50	5	O	Dipping	Embodiment Example

Test results mentioned above are shown in Table 29. The following facts are found from the table.

(1) Test samples having no Fe-Ni-O film formed thereon are inferior in press formability, spot weldability, adhesiveness and chemical treatability (NO 1 and NO 2). Although Fe-Ni-O film is formed, test samples having pH less than 10 are slightly inferior in press formability (NO 3 and NO 4).

(2) In the embodiment examples, press formability, spot weldability, adhesiveness and chemical treatability are improved (NO 5 to NO 14). Press formability is largely improved when the solution for alkali treatment has a large value of pH. These advantageous effects do not vary regardless of an order of temper rolling and alkali treatment in the preliminary treatment.

Table 29

No.	Frictional Coefficient	Spot Weldability Number of Continuous spot-welding runs	Adhesiveness Strength kg/25 mm	Chemical treatability	Test Sample
1	0.150	2500	8.0	—	Comparative Example
2	0.145	2500	10.0	—	Comparative Example
3	0.125	5000	12.0	O	Comparative Example
4	0.125	5000	12.5	O	Comparative Example
5	0.120	5500	12.0	O	Embodiment Example
6	0.120	5500	12.0	O	Embodiment Example
7	0.115	5500	12.5	O	Embodiment Example
8	0.115	5500	12.5	O	Embodiment Example
9	0.110	5500	12.5	O	Embodiment Example
10	0.110	5500	12.5	O	Embodiment Example
11	0.105	5500	12.5	O	Embodiment Example
12	0.105	5500	12.5	O	Embodiment Example
13	0.105	5500	12.5	O	Embodiment Example
14	0.105	5500	12.5	O	Embodiment Example

(2 OF TEST 1)

As shown in Table 4, test conditions are such that zinciferous plated steel sheets of which kind of plating is identified by marks A (representing alloyed zinc dip-plating) are subjected to temper rolling before or after alkali treatment at an elongation ratio of 5.5 %, alkali treating is conducted by dipping them in an aqueous solution of NaOH having constant pH of 12.0 at a temperature of 50 °C for a period of time of 5 seconds, and subsequently, on completion of the preliminary treatment, Fe-Ni-O film is formed on the surface of each zinciferous plated steel sheet by dipping the latter in the aqueous solution containing FeCl₂ and NiCl₂.

Table 30

No.	Kind of plating	Conditions for Temper Rolling		Conditions for Alkali Treatment				Fe-Ni-O film		Test Sample
		Elongation Rate %	Before or After Alkali Treatment	Solution Component	pH	Method of Treatment	Temperature (°C)	Time (s)	Presence or Absence of Film	
15	A	0.0	Before	NaOH	12.0	Dipping	50	5	O	Dipping Comparative Example
17	A	0.2	Before	NaOH	12.0	Dipping	50	5	O	Dipping Comparative Example
18	A	0.2	After	NaOH	12.0	Dipping	50	5	O	Dipping Comparative Example
19	A	0.3	Before	NaOH	12.0	Dipping	50	5	O	Dipping Embodiment Example
20	A	0.3	After	NaOH	12.0	Dipping	50	5	O	Dipping Embodiment Example
21	A	0.7	Before	NaOH	12.0	Dipping	50	5	O	Dipping Embodiment Example
22	A	0.7	After	NaOH	12.0	Dipping	50	5	O	Dipping Embodiment Example
23	A	1.0	Before	NaOH	12.0	Dipping	50	5	O	Dipping Embodiment Example
24	A	1.0	After	NaOH	12.0	Dipping	50	5	O	Dipping Embodiment Example
25	A	3.0	Before	NaOH	12.0	Dipping	50	5	O	Dipping Embodiment Example
26	A	3.0	After	NaOH	12.0	Dipping	50	5	O	Dipping Embodiment Example
27	A	5.0	Before	NaOH	12.0	Dipping	50	5	O	Dipping Embodiment Example
28	A	5.0	After	NaOH	12.0	Dipping	50	5	O	Dipping Embodiment Example
29	A	5.5	Before	NaOH	12.0	Dipping	50	5	O	Dipping Comparative Example
30	A	5.5	After	NaOH	12.0	Dipping	50	5	O	Dipping Comparative Example

(Note) Test sample No. 16 is not shown in this Table

Results of the tests mentioned above are shown in Table 31. The following facts are found from this table.

(1) When temper rolling of the preliminary treatment is conducted at an elongation ratio less than 0.3 %, properties of press formability are insufficiently improved, although Fe-Ni-O film is formed on the surface of each zinciferous plated steel sheet (NO 15 to NO 18). When the elongation ratio exceeds 5.0 %, each zinciferous plated steel sheet is superior in press formability, spot weldability, adhesiveness and chemical treatability but mechanical properties of the zinciferous plated steel sheet are inferior (NO 29 and NO 30).

(2) On the contrary, in the embodiment examples, press formability, spot weldability, properties of adhesiveness and properties of each zinciferous plated steel sheet are improved (NO 19 to NO 28). Press formability of the latter is largely improved when temper rolling is conducted at a large elongation ratio. These advantageous effects are not unchangeably obtained during preliminary treatment of the steel sheet regardless of an order of temper rolling and alkali treatment.

Table 31

No.	Frictional Coefficient	Spot-Weldability Number of Continuous spot-welding runs	Adhesiveness Strength kg/25 mm	Properties of Formation Treatment	Remark	Test Sample
15	0.130	5500	12.5	O	-	Comparative Example
17	0.125	5500	12.5	O	-	Comparative Example
18	0.125	5500	12.5	O	-	Comparative Example
19	0.120	5500	12.5	O	-	Embodiment Example
20	0.120	5500	12.5	O	-	Embodiment Example
21	0.110	5500	12.5	O	-	Embodiment Example
22	0.110	5500	12.5	O	-	Embodiment Example
23	0.105	5500	12.5	O	-	Embodiment Example
24	0.105	5500	12.5	O	-	Embodiment Example
25	0.100	5500	12.5	O	-	Embodiment Example
26	0.100	5500	12.5	O	-	Embodiment Example
27	0.09	5500	12.5	O	-	Embodiment Example
28	0.09	5500	12.5	O	-	Embodiment Example
29	0.09	5500	12.5	O	Material Deteriorated	Comparative Example
30	0.09	5500	12.5	O	Material Deteriorated	Comparative Example
(note) Test sample No. 16 is not shown in this Table						

(3 of TEST 1)

As shown in Table 32, test conditions are such that zinciferous plated steel sheets of which kind of plating is identified by marks A (representing alloyed zinc dip-plating) are subjected to temper rolling at a constant elongation ratio of 0.7 %, alkali treatment is conducted by dipping them in an aqueous solution having constant pH of 12.0 (a part of them is dipped in an acid solution having pH of 20) at a temperature of 50 °C for a period of time of 5 seconds (the aqueous solution is sprayed to a part of them), and subsequently, on completion of the preliminary treatment, Fe-Ni-O film is formed on the surface of each zinciferous plated steel sheet by dipping the latter in the aqueous solution containing FeCl₂ and NiCl₂ (the aqueous solution is given to a part of the zinciferous plated steel sheets by spraying, electrolyzing

or vapor depositing).

Table 32

No.	Kind of Plating	Conditions for Temper Rolling		Conditions for Alkali Treatment					Fe-Ni-O film		Test Sample
		Elongation Rate %	Before or After Alkali Treatment	Solution		Method of Treatment	Temperature (°C)	Time (s)	Presence or Absence of Filmation	Method of Film Formation	
				Component	pH						
31	A	0.7	Before	H ₂ SO ₄	2.0	Dipping	50	5	0	Dipping	Comparative Example
32	A	0.7	Before	HCl	2.0	Dipping	50	5	0	Dipping	Comparative Example
33	A	0.7	Before	NaOH	12.0	Spraying	50	5	0	Dipping	Embodiment Example
34	A	0.7	Before	KOH	12.0	Dipping	50	5	0	Dipping	Embodiment Example
35	A	0.7	Before	Na ₂ SiO ₄	12.0	Dipping	50	5	0	Dipping	Embodiment Example
36	A	0.7	Before	Mg(OH) ₂	12.0	Dipping	50	5	0	Dipping	Embodiment Example
37	A	0.7	Before	LiOH	12.0	Dipping	50	5	0	Dipping	Embodiment Example
38	A	0.7	Before	Na ₂ PO ₄	12.0	Dipping	50	5	0	Dipping	Embodiment Example
39	A	0.7	Before	NaOH	12.0	Dipping	50	5	0	Spraying	Embodiment Example
40	A	0.7	Before	NaOH	12.0	Dipping	50	5	0	Electrolyzing	Embodiment Example
41	A	0.7	Before	NaOH	12.0	Dipping	50	5	0	Vapor Deposit- ing	Embodiment Example

Results of the tests mentioned above are shown in Table 33. The following facts are found from this table.

- (1) When the preliminary treatment is conducted by using the acid aqueous solution containing acid components, properties of press formability is insufficiently improved (NO 31 and NO 32).
- (2) On the contrary, in the examples, press formability, spot weldability and adhesiveness of each zinciferous plated steel sheet are improved (NO 33 to NO 41).

Table 33

No.	Frictional Coefficient	Spot Weldability Number of Continuous spot-welding runs	Adhesiveness Strength kg/25 mm	Chemical treatability	Test Sample
31	0.130	5000	12.5	O	Comparative Example
32	0.130	5000	12.5	O	Comparative Example
33	0.110	5500	12.5	O	Embodiment Example
34	0.110	5500	12.5	O	Embodiment Example
35	0.110	5500	12.5	O	Embodiment Example
36	0.110	5500	12.5	O	Embodiment Example
37	0.110	5500	12.5	O	Embodiment Example
38	0.110	5500	12.5	O	Embodiment Example
39	0.110	5500	12.5	O	Embodiment Example
40	0.110	5500	12.5	O	Embodiment Example
41	0.110	5500	12.5	O	Embodiment Example

[Test 2]

As shown in Table 34, testing conditions are such that each test is performed by using zinciferous plated steel sheets of which kind of plating is changed to B, C, D, F and G. In the embodiment examples, temper rolling is conducted at an elongation ratio of 0.7 % before alkali treatment, preliminary treatment is conducted by dipping each zinciferous plated steel sheet in an aqueous solution of NaON having pH of 12.0 at a temperature of 50 °C for a period of 5 seconds, and on completion of the preliminary treatment, Fe-Ni-O film is formed on the surface of zinciferous plated steel sheet by dipping it in an aqueous solution containing FeCl_2 and NiCl_2 . In comparative examples, the case that all of temper rolling, alkali treatment and formation of Fe-Ni-O film are not conducted and the case that alkali treatment is conducted but temper rolling is not conducted and Fe-Ni-O film is formed are comparatively tested.

Table 34

No.	Kind of Plating	Conditions for Temper Rolling		Conditions for Alkali Treatment					Fe-Ni-O film		Test Sample
		Elongation Rate %	Before or After Alkali Treatment	Solution		Method of Treatment	Temperature (°C)	Time (s)	Presence or Absence of Film	Method of Film Formation	
				Component	pH						
42	B	0.0	-	-	-	-	-	-	X	-	Comparative Example
43	B	0.0	-	NaOH	12.0	Dipping	50	5	O	Dipping	Comparative Example
44	B	0.7	Before	NaOH	12.0	Dipping	50	5	O	Dipping	Embodiment Example
45	C	0.0	-	-	-	-	-	-	X	-	Comparative Example
46	C	0.0	-	NaOH	12.0	Dipping	50	5	O	Dipping	Comparative Example
47	C	0.7	Before	NaOH	12.0	Dipping	50	5	O	Dipping	Embodiment Example
48	D	0.0	-	-	-	-	-	-	X	-	Comparative Example
49	D	0.0	-	NaOH	12.0	Dipping	50	5	O	Dipping	Comparative Example
50	D	0.7	Before	NaOH	12.0	Dipping	50	5	O	Dipping	Embodiment Example
51	E	0.0	-	-	-	-	-	-	X	-	Comparative Example
52	E	0.0	-	NaOH	12.0	Dipping	50	5	O	Dipping	Comparative Example
53	E	0.7	Before	NaOH	12.0	Dipping	50	5	O	Dipping	Embodiment Example
54	F	0.0	-	-	-	-	-	-	X	-	Comparative Example
55	F	0.0	-	NaOH	12.0	Dipping	50	5	O	Dipping	Comparative Example
56	F	0.7	Before	NaOH	12.0	Dipping	50	5	O	Dipping	Embodiment Example
57	G	0.0	-	-	-	-	-	-	X	-	Comparative Example
58	G	0.0	-	NaOH	12.0	Dipping	50	5	O	Dipping	Comparative Example
59	G	0.7	Before	NaOH	12.0	Dipping	50	5	O	Dipping	Embodiment Example

Results of the tests mentioned above are shown in Table 35. The following facts are found from this table.

(1) In the case that all of temper rolling, alkali treatment and formation of Fe-Ni-O film are not performed regardless of the kind of plating, press formability, spot weldability and adhesiveness of each zinciferous plated steel sheet are inferior (NO 42, NO 45, NO 48, NO 51, NO 54 and NO 57). In the case that only temper rolling is not performed among the conditions of the present invention, only press formability is improved to some extent because the Fe-Ni-O film is formed on the surface of the plated steel sheet but the improvement is not sufficient (NO 43, NO 46, NO 49, NO 52, NO 55 and NO 58).

(2) On the contrary, in the embodiment examples, press formability, spot weldability and properties of adhesiveness

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are improved (NO 44, NO 47, NO 50, NO 53, NO. 56 and NO 59).

Table 35

No.	Frictional Coefficient	Spot Weldability Number of Continuous spot-welding runs	Adhesiveness Strength kg/25 mm	Chemical Treatability	Test Sample
42	0.180	1500	5.0	O	Comparative Example
43	0.150	1500	6.0	O	Comparative Example
44	0.125	4000	12.5	O	Embodiment Example
45	0.180	2500	6.0	O	Comparative Example
46	0.150	250	7.0	O	Comparative Example
47	0.125	5000	12.5	O	Embodiment Example
48	0.150	3000	8.0	O	Comparative Example
49	0.130	3000	10.0	O	Comparative Example
50	0.110	6000	12.5	O	Embodiment Example
51	0.150	8000	6.0	O	Comparative Example
52	0.130	8000	7.0	O	Comparative Example
53	0.110	10000	12.5	O	Embodiment Example
54	0.150	3000	6.0	O	Comparative Example
55	0.130	3000	7.0	O	Comparative Example
56	0.110	6000	12.5	O	Embodiment Example
57	0.180	1500	5.0	O	Comparative Example
58	0.150	1500	7.0	O	Comparative Example
59	0.125	4000	12.5	O	Embodiment Example

(TEST 3)

As shown on Table 10 and Table 11, test conditions are such that zinciferous plated steel sheets of which kind of plating is identified by marks A (representing alloyed zinc dip-plating) are subjected to temper rolling before or after alkali treatment at an elongation ratio of 0.7 %, alkali treating is conducted by dipping them in an aqueous solution of NaOH having constant pH of 12.0 at a temperature of 50 °C for a period of time of 5 seconds, and subsequently, on completion of the preliminary treatment, Fe-Ni-O film is formed on the surface of each zinciferous plated steel sheet by dipping the latter in the aqueous solution containing FeCl_2 and NiCl_2 . Here, the total concentration of FeCl_2 and NiCl_2 in the aqueous solution is set to a constant value of 200 g/l, and a ratio of a sum of Fe content (wt. %) and Ni content (wt. %) to the Fe content (wt. %) is variously changed within the range of 0 to 1 so that pH of the aqueous solution is set to 2.5 and a temperature of the aqueous solution is maintained at the temperature of 50 °C.

Table 36

No.	Conditions for Temper Rolling		Conditions for Alkali Treatment				Fe-Ni-O Forming Method	Aqueous Solution					Test Sample			
	Kind of Plating	Elongation Rate (%)	Before or After Alkali Treatment	Solution		Treat-ment Method		Tempera- ture (°C)	Time (s)	FeCl ₂ (g/l)	NiCl ₂ (g/l)	Tempera- ture (°C)		Dipp- ing Time	Fe — Fe+Ni	
				Component	pH											
60	A	0.7	Before	NaOH	12.0	Dipping	50	5	Dipping	0.0	200.0	2.5	50	10	0	Comparative Example
61	A	0.7	Before	NaOH	12.0	Dipping	50	5	Dipping	0.7	199	2.5	50	10	0.0035	Embodiment Example
62	A	0.7	Before	NaOH	12.0	Dipping	50	5	Dipping	0.8	199	2.5	50	10	0.004	Embodiment Example
63	A	0.7	Before	NaOH	12.0	Dipping	50	5	Dipping	1.0	199	2.5	50	10	0.005	Embodiment Example
64	A	0.7	Before	NaOH	12.0	Dipping	50	5	Dipping	5.0	195	2.5	50	10	0.025	Embodiment Example
65	A	0.7	Before	NaOH	12.0	Dipping	50	5	Dipping	10.0	190	2.5	50	10	0.05	Embodiment Example
66	A	0.7	Before	NaOH	12.0	Dipping	50	5	Dipping	20.0	180	2.5	50	10	0.1	Embodiment Example
67	A	0.7	Before	NaOH	12.0	Dipping	50	5	Dipping	30.0	170	2.5	50	10	0.15	Embodiment Example
68	A	0.7	Before	NaOH	12.0	Dipping	50	5	Dipping	40.0	160	2.5	50	10	0.2	Embodiment Example
69	A	0.7	Before	NaOH	12.0	Dipping	50	5	Dipping	50.0	150	2.5	50	10	0.25	Embodiment Example
70	A	0.7	Before	NaOH	12.0	Dipping	50	5	Dipping	60.0	140	2.5	50	10	0.3	Embodiment Example
71	A	0.7	Before	NaOH	12.0	Dipping	50	5	Dipping	80.0	120	2.5	50	10	0.4	Embodiment Example
72	A	0.7	Before	NaOH	12.0	Dipping	50	5	Dipping	100.0	100	2.5	50	10	0.5	Embodiment Example
73	A	0.7	Before	NaOH	12.0	Dipping	50	5	Dipping	120.0	80	2.5	50	10	0.6	Embodiment Example
74	A	0.7	Before	NaOH	12.0	Dipping	50	5	Dipping	140.0	60	2.5	50	10	0.7	Embodiment Example
75	A	0.7	Before	NaOH	12.0	Dipping	50	5	Dipping	160.0	40	2.5	50	10	0.8	Embodiment Example
76	A	0.7	Before	NaOH	12.0	Dipping	50	5	Dipping	180.0	20	2.5	50	10	0.9	Embodiment Example
77	A	0.7	Before	NaOH	12.0	Dipping	50	5	Dipping	185.0	15	2.5	50	10	0.925	Embodiment Example
78	A	0.7	Before	NaOH	12.0	Dipping	50	5	Dipping	200.0	0	2.5	50	10	1	Comparative Example

Table 37

No.	Conditions for Temper Rolling		Conditions for Alkali Treatment					Fe-Ni-O		Aqueous Solution					Test Sample	
	Kind of Plating	Elongation Rate (%)	Before or After Alkali Treatment	Solution		Treatment Method	Temperature (°C)	Time (s)	Film Forming Method	FeCl ₂ (g/l)	NiCl ₂ (g/l)	pH	Temperature (°C)	Dipping Time		Fe — Fe+Ni
				Component	pH											
79	A	0.7	After	NaOH	12.0	Dipping	50	5	Dipping	0.0	200.0	2.5	50	10	Comparative Example	
80	A	0.7	After	NaOH	12.0	Dipping	50	5	Dipping	0.7	199	2.5	50	10	Embodiment Example	
81	A	0.7	After	NaOH	12.0	Dipping	50	5	Dipping	0.8	199	2.5	50	10	Embodiment Example	
82	A	0.7	After	NaOH	12.0	Dipping	50	5	Dipping	1.0	199	2.5	50	10	Embodiment Example	
83	A	0.7	After	NaOH	12.0	Dipping	50	5	Dipping	5.0	195	2.5	50	10	Embodiment Example	
84	A	0.7	After	NaOH	12.0	Dipping	50	5	Dipping	10.0	190	2.5	50	10	Embodiment Example	
85	A	0.7	After	NaOH	12.0	Dipping	50	5	Dipping	20.0	180	2.5	50	10	Embodiment Example	
86	A	0.7	After	NaOH	12.0	Dipping	50	5	Dipping	30.0	170	2.5	50	10	Embodiment Example	
87	A	0.7	After	NaOH	12.0	Dipping	50	5	Dipping	40.0	160	2.5	50	10	Embodiment Example	
88	A	0.7	After	NaOH	12.0	Dipping	50	5	Dipping	50.0	150	2.5	50	10	Embodiment Example	
89	A	0.7	After	NaOH	12.0	Dipping	50	5	Dipping	60.0	140	2.5	50	10	Embodiment Example	
90	A	0.7	After	NaOH	12.0	Dipping	50	5	Dipping	80.0	120	2.5	50	10	Embodiment Example	
91	A	0.7	After	NaOH	12.0	Dipping	50	5	Dipping	100.0	100	2.5	50	10	Embodiment Example	
92	A	0.7	After	NaOH	12.0	Dipping	50	5	Dipping	120.0	80	2.5	50	10	Embodiment Example	
93	A	0.7	After	NaOH	12.0	Dipping	50	5	Dipping	140.0	60	2.5	50	10	Embodiment Example	
94	A	0.7	After	NaOH	12.0	Dipping	50	5	Dipping	160.0	40	2.5	50	10	Embodiment Example	
95	A	0.7	After	NaOH	12.0	Dipping	50	5	Dipping	180.0	20	2.5	50	10	Embodiment Example	
96	A	0.7	After	NaOH	12.0	Dipping	50	5	Dipping	185.0	15	2.5	50	10	Embodiment Example	
97	A	0.7	After	NaOH	12.0	Dipping	50	5	Dipping	200.0	0	2.5	50	10	Comparative Example	

Results of tests mentioned above are shown in Table 38 and Table 39. The following facts are found from these tables.

- (1) In the comparative examples, in the case that the ratio of Fe/(Fe + Ni) applicable to the aqueous solution for

forming Fe-Ni-O film is set to 0 and thus Ni-O film is formed, press formability and properties of each zinciferous plated steel sheet are inferior (NO 60 and NO 79). On the other hand, in the case that $\text{Fe}/(\text{Fe} + \text{Ni})$ is set to 1 and thus the Fe-O film is formed, press formability and sot weldability are inferior (NO 78 and NO 97).

(2) On the contrary, in the examples, press formability, adhesiveness and chemical treatability are improved (NO 61 to NO 77 and NO 80 to NO 96). Especially, in the case that the ratio $\text{Fe}/(\text{Fe} + \text{Ni})$ is within the range of 0.04 to 0.9, the foregoing properties are largely improved. These advantageous effects are not changed regardless of an order of temper rolling and alkali treatment to be conducted in the preliminary treatment for the steel sheets (NO 78 and NO 97).

Table 38

No.	Frictional Coefficient	Spot Weldability Number of Continuous Spot-welding runs	Adhesiveness Strength kg/25 mm	Chemical Treatability	Test Sample
60	0.135	5500	6.0	O	Comparative Example
61	0.130	5500	10.0	O	Embodiment Example
62	0.120	5500	12.0	O	Embodiment Example
63	0.110	5500	12.5	O	Embodiment Example
64	0.110	5500	12.5	O	Embodiment Example
65	0.110	5500	12.5	O	Embodiment Example
66	0.110	5000	12.5	O	Embodiment Example
67	0.110	5000	12.5	O	Embodiment Example
68	0.110	5500	12.5	O	Embodiment Example
69	0.110	5500	12.5	O	Embodiment Example
70	0.110	5500	12.5	O	Embodiment Example
71	0.110	5500	12.5	O	Embodiment Example
72	0.110	5500	12.5	O	Embodiment Example
73	0.110	5500	12.5	O	Embodiment Example
74	0.110	5000	12.5	O	Embodiment Example
75	0.120	4500	12.5	O	Embodiment Example
76	0.120	4000	12.5	O	Embodiment Example
77	0.130	3000	12.5	O	Embodiment Example
78	0.135	2500	12.5	O	Comparative Example

Table 39

No.	Frictional Coefficient	Spot Weldability Number of Continuous spot-welding runs	Adhesiveness Strength kg/25 mm	Chemical Treatability	Test Sample
79	0.135	5500	6.0	O	Comparative Example
80	0.130	5500	10.0	O	Embodiment Example
81	0.120	5500	12.0	O	Embodiment Example
82	0.110	5500	12.5	O	Embodiment Example
83	0.110	5500	12.5	O	Embodiment Example
84	0.110	5500	12.5	O	Embodiment Example
85	0.110	5000	12.5	O	Embodiment Example
86	0.110	5000	12.5	O	Embodiment Example
87	0.110	5500	12.5	O	Embodiment Example
88	0.110	5500	12.5	O	Embodiment Example
89	0.110	5500	12.5	O	Embodiment Example
90	0.110	5500	12.5	O	Embodiment Example
91	0.110	5500	12.5	O	Embodiment Example
92	0.110	5500	12.5	O	Embodiment Example
93	0.110	5000	12.5	O	Embodiment Example
94	0.120	4500	12.5	O	Embodiment Example
95	0.120	4000	12.5	O	Embodiment Example
96	0.130	3000	12.5	O	Embodiment Example
97	0.135	2500	12.5	O	Comparative Example

Since the method of the present invention is performed in the above-mentioned manner, properties of Fe-Ni-O film formed on the surface of the plating layer of zinciferous plated steel sheet are improved, and moreover, since Fe-Ni-O film is hard in comparison with the zinc or zinc alloy plating layer and has a high temperature point, sliding resistance

between the surface of plating layer and the press forming die is reduced at the time of press forming, causing the zinciferous plated steel sheet to be easily received in the press forming die with the result that the press formability is improved. In addition, continuous spot-weldability during spot welding are improved owing to the presence of Fe-Ni-O film. Additionally, properties of the Fe-Ni-O plated steel sheet are improved owing to the presence of the Fe-Ni-O film. As will be apparent from the above description, the present invention can provide a method for producing a zinciferous plated steel sheet with excellent properties of press formability and spot weldability as well as excellent adhesiveness, resulting in very usable industrial effects being assured.

EMBODIMENT 7

The present inventors have made continued research to obtain several results described later. Namely, improved press formability can be attained by the formation of a Fe-Ni-O film on the plating layer disposed on an alloyed zinc dip-plated steel sheet and provided with a surface alloy phase that is of a ζ or $\delta 1$ phase.

It will be reasoned here why the above specified construction can provide an alloyed zinc dip-plated steel sheet having excellent press formability.

Insufficient press formability inherent to an alloyed zinc dip-plated steel sheet is due to the fact that when the surface alloy phase present on a plating layer is of a η or ζ phase, a cohesive phenomenon takes place between a η or ζ phase of a soft nature and of a low melting point and a mating mold at elevated surface pressure, resulting in increased sliding resistance. The surface alloy phase if being of a $\eta 1$ phase is harder in nature and higher in melting point than the η and ζ phases, but is still more susceptible to sticking than a cold-rolled steel sheet.

For such problems to be solved, it is effective to provide a film of a higher hardness and of a higher melting point than a Fe-Zn alloy phase. A Fe-Ni-O film according to the present invention is high in hardness and high in melting point. When applied on to an alloyed zinc dip-plated steel sheet, this film acts to reduce such resistance as tending to occur on sliding movement of the plating layer with respect to the associated pressure mold, thus allowing the steel sheet to easily slide into the mold so that press formability is improved.

Furthermore, where a ζ phase of a low Fe content is required to be disposed on the plating layer, a brittle ζ phase can be prevented against generation with the result that powdering resistance is improved at the same time. Where a $\delta 1$ phase of a high Fe content is desired to be formed on the plating layer, a η phase of a soft nature and of a low melting point can be prevented from getting generated, whereby flaking resistance is simultaneously improved.

Alloyed zinc dip-plated steel sheets in common use are poor in respect of continuous spot-weldability during spot welding when compared to a cold-rolled steel sheet. This is because zinc having melted at the time of spot welding makes a reactive contact with a copper electrode to generate a brittle alloy layer which would deteriorate the electrode with violence.

It is generally recognized that continuous spot-weldability could be effectively improved by forming a high-melting film on the plating layer of an alloyed zinc dip-plated steel sheet. To gain improved spot weldability of the steel sheet, the present inventors have made studies of a variety of films and have now found that a film derived particularly from an oxide of Ni is suited for that purpose. Although the reasoning is not exactly unknown, it is thought that Ni would react with Zn to generate a high-melting Zn-Ni alloy and that because of its extremely high melting point and also of its semiconductive properties, Ni would exhibit electrical conductivity to rather high a degree among the various films.

Conventional alloyed zinc dip-plated steel sheets are known to be lower in adhesiveness than a cold-rolled steel sheet, but little has been elucidated about the cause. As a result of studies made by the present inventors, it has been found that adhesiveness is dominated by the composition of an oxide film deposited on a steel sheet. That is, the oxide film is predominantly of a Fe oxide in the cold-rolled steel sheet, while the oxide film is mainly of a Zn oxide in the alloyed zinc dip-plated steel sheet. Adhesiveness varies with the composition of each of the two different films, and the Zn oxide has proved inferior in this physical property to the Fe oxide. As contemplated under the present invention, therefore, adhesiveness can be improved by the formation of a Fe oxide-containing film on the alloyed zinc dip-plated steel sheet.

Conventional alloyed zinc hot-plated steel sheets are insufficient in regard to chemical treatability as compared to a cold-rolled steel sheet. This is attributable to the fact that since Zn present on the steel sheet is high in its concentration, a crystal of a phosphate film to be formed is coarse and irregular and that two phosphate crystals used in both of the steel sheets are different from each other. In the case of the cold-rolled steel plate, the phosphate crystal is based mainly on phosphofillite ($\text{Zn}_2\text{Fe}(\text{PO}_4)_3 \cdot 4\text{H}_2\text{O}$). Where the Zn concentration is high on a steel sheet, the phosphate crystal is composed predominantly of phobite ($\text{Zn}_3(\text{PO}_4)_3 \cdot 4\text{H}_2\text{O}$) which is rather poor as to secondary adhesiveness in warm water after painting. The reason behind this is that owing to too low a concentration of Fe in the phosphate film, the chemically treated film causes condensation when exposed to a wetting environment after painting, inviting lost adhesiveness to the steel sheet.

For the chemically treated film to be prevented against condensation, it is effective to incorporate such metals as of Fe, Ni and the like into a phosphate crystal. With a Fe-Ni-O film provided as called for by the present invention, Ni and Fe can incorporate into a phosphate crystal, bringing about a chemically treated film of satisfactory adhesiveness and besides a dense regular phosphate crystal, whereby secondary adhesiveness in warm water as well as corrosion

resistance has been found to be improved.

As previously mentioned, it has been found that an alloyed zinc dip-plated steel sheet can be obtained by properly forming on its plating layer a combination film (hereunder called a Fe-Ni-O film) composed at least of metals of Ni and Fe and oxides of Ni and Fe, which steel sheet is excellent in press formability, spot weldability, adhesiveness and chemical treatability and also in deep drawability. More specifically, one essential requirement of the present invention lies in the provision of the above Fe-Ni-O film on the plating layer.

This invention has been completed based on the foregoing findings. An alloyed zinc dip-plated steel sheet of the first manner comprises a plating layer disposed on at least one surface thereof and having a chemical composition comprised of 6 - 11 wt. % of Fe and as the balance Zn and unavoidable impurities, characterized in that the plating layer is provided with a surface alloy phase which is of ζ phase, and the plating layer has a coating weight of 20 - 100 g/m² and includes a Fe-Ni-O film formed thereon.

An alloyed zinc dip-plated steel sheet of the second manner, characterized in that, in the invention recited in the first manner, the Fe-Ni-O film has a coating weight of 10 - 1500 mg/m² in terms of the total weight of all of the metallic elements contained therein, the content of Fe (wt. %) in the Fe-Ni-O film is in a ratio of 0.004 - 0.9 with respect to the sum of the content of Fe (wt. %) and the content of Ni (wt. %) in the Fe-Ni-O film, and the Fe-Ni-O film contains oxygen in an amount of 0.5 - 10 wt. %.

An alloyed zinc dip-plated steel sheet according to the third manner comprises a plating layer disposed on at least one surface thereof and having a chemical composition comprised of 9 - 14 wt. % of Fe and as the balance Zn and unavoidable impurities, characterized in that the plating layer is provided with a surface alloy phase which is of a $\delta 1$ phase, and the plating layer has a coating weight of 20 - 100 g/m² and includes a Fe-Ni-O film formed thereon.

An alloyed zinc dip-plated steel sheet of the fourth manner, characterized in that, in the third manner, the Fe-Ni-O film has a coating weight of 10 - 1500 mg/m² in terms of the total weight of all of the metallic elements contained therein, the content of Fe (% by weight) in the Fe-Ni-O film is in a ratio of 0.004 - 0.9 with respect to the sum of the content of Fe (wt. %) and the content of Ni (wt. %) in the Fe-Ni-O film, and the Fe-Ni-O film contains oxygen in an amount of 0.5 - 10 wt. %.

Now, the following explanations are given to account for specific limitations imposed, as noted above in the practice of the present invention, upon the alloyed zinc dip-plating layer deposited as an undercoat on the steel sheet and the film formed as an overcoat on the plating layer.

(1) Alloyed Zinc Dip-Plating layer

[When Surface Alloy Phase is of a ζ Phase]

The content of Fe is more than 6 wt. % as less than that content is ineffective to form a ζ phase on the plating layer. Conversely, contents of Fe above 11 wt. % should be avoided to preclude formation of a Γ phase with increased thickness. The Γ phase so formed thick leads to impaired powdering resistance, hence marred press formability, even with a Fe-Ni-O film formed on the plating layer.

Accordingly, the content of Fe in the alloyed zinc dip-plating layer should be in the range of 6 - 11 wt. %.

[When Surface Alloy Phase is of a $\delta 1$ Phase]

The content of Fe in the alloyed zinc dip-plating layer exceeds 9 wt. % since less than that content fails to form a $\delta 1$ phase on the plating layer. Even where a $\delta 1$ phase is provided on the plating layer, contents of Fe above 14 wt. % render the resulting Γ phase large in thickness. The Γ phase thus made thick-walled adversely affects powdering resistance and hence press formability even a Fe-Ni-O film provided on the plating layer.

Thus, the content of Fe in the alloyed zinc dip-plating layer should be in the range of 9 - 14 wt. %.

[Coating weight of Alloyed zinc dip-plating layer]

The coating weight is limited to a range of 20 - 100 g/m². Below 20 g/m² fails to gain sufficient corrosion resistance, while above 100 g/m² causes a Γ phase to excessively grow with large thickness in an alloying step in which Fe is added in an amount of more than 6 wt. % in an alloyed zinc dip-plating layer. The latter case leaves the problem that, even if the present invention is practiced, adequate powdering resistance cannot be attained.

Fe only is specifically represented herein as a component of the alloyed zinc dip-plating layer. Various other metals such as Al, Pb, Cd, Sn, In, Li, Sb, As, Bi, Mg, La, Ca, Ti, Zr, Ni, Co, Cr, Mn, P, S, O and the like may be used so long as they are added in limited amounts to the plating layer or made to unavoidably intrude into the layer. These metals exert no significant effect on those advantages accruing from the present invention. As for Al, for example, this metal has been added in an amount of about 0.1 wt. % to a plating bath in current practice, and hence, may be made to necessarily enter the resultant plating layer.

(2) Fe-Ni-O Film

[Coating weight of Fe-Ni-O Film]

5 The coating weight of the Fe-Ni-O film, if less than 10 mg/m² in terms of the total weight of all the metallic elements, fails to sufficiently improve press formability, and if more than 1500 mg/m², produce no better results in further improvement in such physical property.

The coating weight of the Fe-Ni-O film should, therefore, be preferably in the range of 10 - 1500 mg/m² in terms of the total weight of all the metals in the plating layer.

10 To set the coating weight of the Fe-Ni-O film to be within that range, a length of time for treatment can be adjusted when a salt concentration is held constant in a treating liquid for use in film formation, and a salt concentration in the treating liquid can be adjusted when the treatment time is held constant from equipment standpoints and also with pH and temperature conditions controlled to advantage.

15 [Ratio of Fe Content to Sum of Fe and Ni Contents in Fe-Ni-O Film]

An appropriate content of Fe in a Fe-Ni-O film brings about improved adhesiveness. The better adhesiveness, the higher surface potential of a metal is. Fe is among such metals as of the highest surface potential, and thus, adhesiveness is further improved with increasing contents of Fe. In order to achieve improved adhesiveness, it is necessary that 20 Fe be at least substantially present in the film. To this end, the ratio of a Fe content (wt. %) to the sum of a Fe content (wt. %) and a Ni content (wt. %) in the Fe-Ni-O film (hereunder called Fe/(Fe + Ni) in the film) should be more than 0. Also notably, above 0.004 of Fe/(Fe + Ni) in the film contributes greatly to enhanced adhesiveness.

On the other hand, Ni needs to be substantially contained in the film, and Fe/(Fe + Ni) should not exceed 1. Below 0.9 of Fe/(Fe + Ni) in the film further improves spot weldability.

25 Accordingly, Fe should be contained in the Fe-Ni-O film, preferably in a Fe/(Fe + Ni) of 0.004 - 0.9.

[Content of Oxygen in Fe-Ni-O Film]

30 An appropriate content of oxygen in the Fe-Ni-O film contributes to improved press formability and spot weldability. It is required, to this end, that oxygen be at least substantially contained in the film, and the oxygen content should be more than 0 wt. %. Oxygen contents of above 0.5 wt. % in the Fe-Ni-O film are conducive to highly improved press formability.

Oxygen contents if below 10 wt. % show further improvements in spot weldability and chemical treatability. Thus, oxygen should be contained in the Fe-Ni-O film preferably in a limited range of 0.5 - 10 wt. %.

35 Even if the Fe-Ni-O film contains oxides or hydroxides derivable from elements such as Zn, Co, Mn, Mo, Al, Ti, Sn, W, Si, Pb, Ta and the like, or metal themselves which are present in the undercoat or plating layer, the above noted advantages are satisfactorily achievable.

40 In addition, the Fe-Ni-O film disposed as an overcoat in accordance with the present invention is not restricted as to the preparation method. There may be suitably used various methods such as substitution plating, dip plating in an oxidizing agent-containing aqueous solution, cathodic or anodic electrolyzation in an oxidizing agent-containing aqueous solution, spraying of a given aqueous solution, roll coating and the like, laser assisted CVD, photon assisted CVD, vacuum deposition and gaseous phase plating such as sputtering deposition.

45 The Fe-Ni-O film discussed hereinabove is formed on a plating layer disposed on at least one surface of an alloyed zinc dip-plated steel sheet. Steel sheets having carried such a film on either one of the surfaces thereof, or such films on both of the surfaces may be selected depending upon the process step in which to employ the steel sheet in the manufacture of an automobile body and upon the region at which to shape the body.

Examples

50 The present invention is further described with reference to examples.

A 0.7 mm-thick, cold-rolled steel sheet was subjected to alloyed zinc dip-plating in known manner and with the coating weight, the content of Fe in a plating layer and the surface alloy phase adjusted to the desired parameters, whereby an alloyed zinc dip-plated steel sheet was produced. A Fe-Ni-O film was thereafter formed on the plating layer by any one of the following three preparation methods.

55 [Preparation Method A]

An alloyed zinc dip-plated steel sheet was cathodically electrolyzed in a solution composed of a mixture of ferrous sulfate and nickel sulfate and containing an oxidizing agent so that a desired Fe-Ni-O film was formed on the plating

layer. Here, the concentration of ferrous sulfate in a 100g/l was varied with that of nickel sulfate held constant. Furthermore, with the pH and temperature of the mixed solution held constant respectively at 2.5 and at 50 °C, aqueous hydrogen peroxide was used as the oxidizing agent, and the oxygen content in the film was varied with various desirable concentrations of the oxidizing agent.

[Preparation Method B]

Sprayed on to an alloyed zinc dip-plated steel sheet was an aqueous solution containing nickel chloride in a 120 g/l concentration and ferrous chloride in varied desired concentrations. Drying was conducted in a mixed atmosphere of air and ozone with a Fe-Ni-O film adjusted in its oxygen content, whereby a desired Fe-Ni-O film was formed on the plating layer.

[Preparation Method C]

An alloyed zinc dip-plated steel sheet was immersed in an aqueous solution containing nickel chloride in a 120 g/l concentration and ferrous chloride in varied desired concentrations and having a pH of 2.5 - 3.5 and a temperature of 50 °C. The coating weight of a Fe-Ni-O film was varied at a desired level by adjustment of dipping time. The content of oxygen in a Fe-Ni-O film was varied, through pH adjustment, within a desired range. To further adjust the oxygen content, a given oxidizing agent was incorporated in a given aqueous solution, and heating was done in a given oxidative atmosphere so that a desired Fe-Ni-O film was formed on the alloyed zinc dip-plated steel sheet.

By formation of Fe-Ni-O films on alloyed zinc dip-plated steel sheets using the above preparation methods, specimens according to the present invention and for comparative purposes were produced. These inventive and comparative specimens were obtained as two separate groups. A first test ("Example 1") was directed to examples related to manners 1 and 3 and a second test ("Example 2") to examples related to manners 2 and 4.

[First Test]

In Tables 40 and 41, the inventive and comparative specimens obtained in the first test are listed in regard to the contents of Fe in the alloyed zinc dip-plating layers, the surface alloy phases on the plating layers, the coating weight, and the preparation methods of Fe-Ni-O films and the presence or absence of the films.

Table 40

Specimen No.	Alloyed Zinc		Dip-Plated Layer		Fe-Ni-O Film		Press Formability		Powder- ing Resist- ance	Spot Weld- ability	Adhesion	Chemical Treatment	
	Fe Content wt. %	Surface Alloy Phase	Plating Deposit mg/m ²	Film Forming Method	Presence/ Absence of Film	Friction Co- efficient	Percentage Change of Outer Diameter						
1	5	η	30	A	O	X	X	X	O	O	O	O	Comparative Example
2	5	η	30	-	X	X	X	X	O	X	X	X	Comparative Example
3	6	η	60	B	O	X	X	X	O	O	O	O	Comparative Example
4	6	η	60	-	X	X	X	X	O	X	X	X	Comparative Example
5	6	ξ	45	C	O	O	O	O	O	O	O	O	Comparative Example
6	6	ξ	45	-	X	X	X	X	O	X	X	X	Comparative Example
7	7	η	30	C	O	X	X	X	O	O	O	O	Comparative Example
8	7	η	30	-	X	X	X	X	O	X	X	X	Comparative Example
9	7	ξ	60	A	O	O	O	X	O	O	X	X	Comparative Example
10	7	ξ	60	-	X	X	X	X	O	X	X	X	Comparative Example
11	8	ξ	60	A	O	O	O	O	O	O	O	O	Comparative Example
12	8	ξ	60	-	X	X	X	X	O	X	X	X	Comparative Example
13	9	ξ	45	B	O	O	O	O	O	O	O	O	Comparative Example
14	9	ξ	45	-	X	X	X	X	O	X	X	X	Comparative Example
15	9	δ	90	A	O	O	O	O	O	O	O	O	Comparative Example
16	9	δ	90	-	X	X	X	X	X	X	X	X	Comparative Example
17	10	ξ	30	C	O	O	O	O	O	O	O	O	Comparative Example
18	10	ξ	30	-	X	X	X	X	O	X	X	X	Comparative Example
19	10	δ	30	B	O	O	O	O	O	O	O	O	Comparative Example
20	10	δ	30	-	X	X	X	X	X	X	X	X	Comparative Example

0: Practically acceptable X: Practically unacceptable

Table 41

Specimen No.	Alloyed Zinc		Dip-plated Layer	Fe-Ni-O Film		Press Formability		Powdering Resistance	Spot Weldability	Adhesion	Chemical Treatment	
	Fe Content (wt. %)	Surface Alloy Phase	Plating Deposit mg/m ²	Film Forming Method	Presence/Absence of Film	Friction Coefficient	Percentage Change of Outer Diameter					
21	11	ξ	60	C	O	O	X	O	X	O	O	Example
22	11	ξ	60	-	X	X		X	X	X	X	Comparative Example
23	11	δ1	60	B	O	O		O	O	O	O	Example
24	11	δ1	60	-	X	X	X	X	X	X	X	Comparative Example
25	12	ξ	45	A	O	O	O	X	O	O	O	Comparative Example
26	12	ξ	45	-	X	X	X	X	X	X	X	Comparative Example
27	12	δ1	60	C	O	O	O	O	O	O	O	Example
28	12	δ1	60	-	X	X	X	X	X	X	X	Comparative Example
29	13	ξ	45	A	O	O	O	X	O	O	O	Comparative Example
30	13	ξ	45	-	X	X	X	X	X	X	X	Comparative Example
31	13	δ1	45	C	O	O	O	O	O	O	O	Example
32	13	δ1	45	-	X	X	X	X	X	X	X	Comparative Example
33	14	ξ	90	A	O	O	O	X	O	O	O	Comparative Example
34	14	ξ	90	-	X	X	X	X	X	X	X	Comparative Example
35	14	δ1	90	C	O	O	O	O	O	O	O	Example
36	14	δ1	90	-	X	X	X	X	X	X	X	Comparative Example
37	15	ξ	60	A	O	O	O	X	O	O	O	Comparative Example
38	15	ξ	60	-	X	X	X	X	X	X	X	Comparative Example
39	15	δ1	60	C	O	O	O	X	O	O	O	Comparative Example
40	15	δ1	60	-	X	X	X	X	X	X	X	Comparative Example

0: Practically acceptable X: Practically unacceptable

Performance evaluation was made of the above specimens in respect of press formability, powdering resistance, spot weldability, adhesiveness and chemical treatability with use of the methods indicated below. Press formability was adjudged based on the friction coefficient of the specimen and also on the percentage change of an outer diameter by a cup deep drawing test.

[Cup Deep Drawing Test]

By a cup deep drawing test, the percentage changes of an outer diameter of a specimen was measured before and after the test.

A 110 mm-diameter disc was blanked from each specimen, followed by cylindrical forming into a die of 53 mm in diameter and 5 mm in shoulder radius at a crease pressing force of 3 tons by use of a punch of 50 mm in diameter and 5 mm in shoulder radius. Noxrust 550 HN manufactured by Nippon Parkerising Co., Ltd. was utilized as a lubricant.

Figure 17 is a schematic perspective view of a specimen after being subjected to a cup deep drawing test. In this figure, designated at 50 is a flange, at D an outer diameter of the flange and at 51 a crack having taken place as a result of cylindrical forming.

The percentage change of the outer diameter of the flange after cup deep drawing was counted from equation below.

$$\text{percentage change of outer diameter (\%)} = \{(110 - D)/110\} \times 100 \quad (1)$$

where

D: outer diameter of flange after testing (mm)

Based on a draw bead test, powdering resistance was evaluated from a peeling (hereunder called "a film peel amount") of a film (an alloyed zinc dip-plating layer and a Fe-Ni-O film) carried on a steel sheet.

[Draw Bead Test]

With use of the following method, the film disposed on the steel sheet was peeled by wiping of a specimen against a bead so that the peel amount was measured.

A test piece of a given shape and of a given dimension was blanked from each specimen, followed by peeling of a plating layer and a Fe-Ni-O film on an asymmetrical side through dissolution with dilute hydrochloric acid and by subsequent degreasing, after which the weight of the test piece was measured. The test piece thus prepared was mounted on a testing machine indicated below.

Figure 18 is a schematic cross-sectional view of a draw bead testing machine used. In this figure, designated at 52 is a test piece, at 53 a bead, at 53a a bead frame, at 54 a die and at 55 a hydraulic device.

Figure 19 is an enlarged view of Figure 18.

As seen in Figure 19, the test piece 52 is positioned between the bead 53 and the bead frame 53a and the die 54 with a test surface (a surface subjected to testing) of the test piece 52 made to face toward the bead 53. Thereafter, upon forward pressing of a press plate 56 by actuation of the hydraulic device 55, the test piece 52 is interposed in pressed relation between the bead frame 13a and the die 54 and then is allowed to abut against a tip of the bead 53. A hydraulic press force P is 500 kgf. With the test surface of the test piece 12 thus abutted against the tip of the bead 13, such test piece is upwardly pulled at normal angle to a longitudinal direction of the bead 53 at a speed of 200 mm/min and in a length of 110 mm.

Illustrated in Figure 20 are the shape and dimension of the bead tip. As is clear from this figure, the bead 53 is of a semi-spherical shape with a tip radius of 1.0 mm and a bead height of 4 mm. Testing was conducted with the test surface coated with a lubricant, Noxrust 550 HN, manufactured by Nippon Parkerising Co., Ltd.

Next, the test piece 52 was degreased and applied on its test surface with an adhesive tape, followed by peeling of the tape and by subsequent further degreasing, and the test piece 52 weight was then measured. The difference of weights before and after testing was counted, from which a peel amount of the film was determined.

From the results shown in Tables 40 and 41, the following facets have been revealed.

The alloyed zinc dip-plated steel sheets falling within the scope of the present invention offer reduced friction coefficient in their films and at the same time improved deep formability, thus showing press formability to a practically acceptable extent.

The film peel amount caused from wiping of a film is practically acceptably small and hence is highly resistant to powdering.

The number of spots when in spot welding is practically acceptably large and hence is highly satisfactory in regard to spot weldability.

The peeloff strength after adhesiveness by use of a resinous adhesive is at a practically acceptable level and hence is highly capable of exhibiting excellent adhesiveness.

The chemically treated zinc phosphate film provides a crystalline state at a practically acceptable level, thus leading to excellent chemical treatability.

In contrast to the inventive steel sheets, the alloyed zinc dip-plated steel sheets outside the scope of the invention

are unsatisfactory with regard to all of friction coefficient, deep drawability, powdering resistance, spot weldability, adhesiveness and chemical treatability.

[Second Test]

A second test will follow with its conditions and results.

In the second test, the coating weight and chemical composition of a Fe-Ni-O film were examined under stricter conditions than in the first test.

In Tables 42 - 47, the inventive and comparative specimens prepared for use in the second test are listed as regards the content of Fe in an alloyed zinc dip-plating layer, the surface alloy phase in the plating layer, the plating deposit, the preparation method of a Fe-Ni-O film, the film coating weight (the reduced total of all of the metallic elements in the film, this being equally applicable to the test results described later), the Fe/(Fe + Ni) in the film and the content of oxygen in the film.

Table 42

Specimen No.	Alloyed Zinc Dip-Plated Layer			Fe-Ni-O Film				
	Fe Content wt. %	Surface Alloy Phase	Plating Deposit g/m ²	Film Forming Method	Film Deposit mg/m ²	Fe/Fe+Ni Content in Film	Oxygen Content wt. %	
41	9	Ξ	60	A	200	0	3.0	Comparative Example
42	9	Ξ	60	A	200	0.002	3.0	Example
43	9	Ξ	60	A	200	0.004	3.0	Example
44	9	Ξ	60	A	200	0.01	3.0	Example
45	9	Ξ	60	A	200	0.02	3.0	Example
46	9	Ξ	60	A	200	0.04	3.0	Example
47	9	Ξ	60	A	200	0.05	3.0	Example
48	9	Ξ	60	A	200	0.08	3.0	Example
49	9	Ξ	60	A	200	0.11	3.0	Example
50	9	Ξ	60	A	200	0.14	3.0	Example
51	9	Ξ	60	A	200	0.17	3.0	Example
52	9	Ξ	60	A	200	0.2	3.0	Example
53	9	Ξ	60	A	200	0.23	3.0	Example
54	9	Ξ	60	A	200	0.24	3.0	Example
55	9	Ξ	60	A	200	0.27	3.0	Example
56	9	Ξ	60	A	200	0.3	3.0	Example
57	9	Ξ	60	A	200	0.33	3.0	Example
58	9	Ξ	60	A	200	0.4	3.0	Example
59	9	Ξ	60	A	200	0.6	3.0	Example
60	9	Ξ	60	A	200	0.8	3.0	Example
61	9	Ξ	60	A	200	0.9	3.0	Example
62	9	Ξ	60	A	200	0.95	3.0	Example
63	9	Ξ	60	A	200	1	3.0	Comparative Example
64	9	Ξ	60	A	200	0.2	0.0	Comparative Example
65	9	Ξ	60	A	200	0.2	0.2	Example
66	9	Ξ	60	A	200	0.2	0.4	Example
67	9	Ξ	60	A	200	0.2	0.5	Example
68	9	Ξ	60	A	200	0.2	1.5	Example
69	9	Ξ	60	A	200	0.2	2	Example
70	9	Ξ	60	A	200	0.2	4	Example
71	9	Ξ	60	A	200	0.2	5	Example
72	9	Ξ	60	A	200	0.2	6	Example
73	9	Ξ	60	A	200	0.2	8	Example
74	9	Ξ	60	A	200	0.2	10	Example
75	9	Ξ	60	A	200	0.2	11	Example
76	9	Ξ	60	A	200	0.2	22	Example

Table 43

Specimen No.	Alloyed Zinc Dip-Plated Layer			Fe-Ni-O Film				
	Fe Content wt. %	Surface Alloy Phase	Plating Deposit g/m ²	Film Forming Method	Film Deposit mg/m ²	Fe/Fe+Ni Content	Oxygen Content wt. %	
77	9	ξ	60	B	200	0.2	0.0	Comparative Example
78	9	ξ	60	B	200	0.2	0.2	Example
79	9	ξ	60	B	200	0.2	0.4	Example
80	9	ξ	60	B	200	0.2	0.5	Example
81	9	ξ	60	B	200	0.2	1.5	Example
82	9	ξ	60	B	200	0.2	2	Example
83	9	ξ	60	B	200	0.2	4	Example
84	9	ξ	60	B	200	0.2	5	Example
85	9	ξ	60	B	200	0.2	6	Example
86	9	ξ	60	B	200	0.2	8	Example
87	9	ξ	60	B	200	0.2	10	Example
88	9	ξ	60	B	200	0.2	11	Example
89	9	ξ	60	B	200	0.2	22	Example

Table 44

Specimen No.	Alloyed Zinc Dip-Plated Layer			Fe-Ni-O Film				
	Fe Content wt. %	Surface Alloy Phase	Plating Deposit g/m ²	Film Forming Method	Film Deposit mg/m ²	Fe/Fe+Ni Content in Film	Oxygen Content wt. %	
90	9	ξ	60	C	0	0.2	1	Comparative Example
91	9	ξ	60	C	5	0.2	1	Example
92	9	ξ	60	C	8	0.2	1	Example
93	9	ξ	60	C	10	0.2	1	Example
94	9	ξ	60	C	30	0.2	1	Example
95	9	ξ	60	C	50	0.2	1	Example
96	9	ξ	60	C	100	0.2	1	Example
97	9	ξ	60	C	200	0.2	1	Example
98	9	ξ	60	C	300	0.2	1	Example
99	9	ξ	60	C	400	0.2	1	Example
100	9	ξ	60	C	500	0.2	1	Example
101	9	ξ	60	C	600	0.2	1	Example
102	9	ξ	60	C	800	0.2	1	Example
103	9	ξ	60	C	1000	0.2	1	Example
104	9	ξ	60	C	1200	0.2	1	Example
105	9	ξ	60	C	1500	0.2	1	Example
106	9	ξ	60	C	1600	0.2	1	Example
107	9	ξ	60	C	200	0.2	0.0	Comparative Example
108	9	ξ	60	C	200	0.2	0.2	Example
109	9	ξ	60	C	200	0.2	0.4	Example
110	9	ξ	60	C	200	0.2	0.5	Example
111	9	ξ	60	C	200	0.2	1.5	Example
112	9	ξ	60	C	200	0.2	2	Example
113	9	ξ	60	C	200	0.2	4	Example
114	9	ξ	60	C	200	0.2	5	Example
115	9	ξ	60	C	200	0.2	6	Example
116	9	ξ	60	C	200	0.2	8	Example
117	9	ξ	60	C	200	0.2	10	Example
118	9	ξ	60	C	200	0.2	11	Example
119	9	ξ	60	C	200	0.2	22	Example

Table 45

Specimen No.	Alloyed Zinc Dip-Plated Layer			Fe-Ni-O Film				
	Fe Content wt. %	Surface Alloy Phase	Plating Deposit g/m ²	Film Forming Method	Film Deposit mg/m ²	Fe/Fe+Ni Content in Film	Oxygen Content wt. %	
120	10	δ 1	60	A	200	0	3.0	Comparative Example
121	10	δ 1	60	A	200	0.002	3.0	Example
122	10	δ 1	60	A	200	0.004	3.0	Example
123	10	δ 1	60	A	200	0.01	3.0	Example
124	10	δ 1	60	A	200	0.02	3.0	Example
125	10	δ 1	60	A	200	0.04	3.0	Example
126	10	δ 1	60	A	200	0.05	3.0	Example
127	10	δ 1	60	A	200	0.08	3.0	Example
128	10	δ 1	60	A	200	0.11	3.0	Example
129	10	δ 1	60	A	200	0.14	3.0	Example
130	10	δ 1	60	A	200	0.17	3.0	Example
131	10	δ 1	60	A	200	0.2	3.0	Example
132	10	δ 1	60	A	200	0.23	3.0	Example
133	10	δ 1	60	A	200	0.24	3.0	Example
134	10	δ 1	60	A	200	0.27	3.0	Example
135	10	δ 1	60	A	200	0.3	3.0	Example
136	10	δ 1	60	A	200	0.33	3.0	Example
137	10	δ 1	60	A	200	0.4	3.0	Example
138	10	δ 1	60	A	200	0.6	3.0	Example
139	10	δ 1	60	A	200	0.8	3.0	Example
140	10	δ 1	60	A	200	0.9	3.0	Example
141	10	δ 1	60	A	200	0.95	3.0	Example
142	10	δ 1	60	A	200	1	3.0	Comparative Example
143	10	δ 1	60	A	200	0.2	0.0	Example
144	10	δ 1	60	A	200	0.2	0.2	Example
145	10	δ 1	60	A	200	0.2	0.4	Example
146	10	δ 1	60	A	200	0.2	0.5	Example
147	10	δ 1	60	A	200	0.2	1.5	Example
148	10	δ 1	60	A	200	0.2	2	Example
149	10	δ 1	60	A	200	0.2	4	Example
150	10	δ 1	60	A	200	0.2	5	Example
151	10	δ 1	60	A	200	0.2	6	Example
152	10	δ 1	60	A	200	0.2	8	Example
153	10	δ 1	60	A	200	0.2	10	Example
154	10	δ 1	60	A	200	0.2	11	Example
155	10	δ 1	60	A	200	0.2	22	Example

Table 46

Specimen No.	Alloyed Zinc Dip-Plated Layer			Fe-Ni-O Film				
	Fe Content wt. %	Surface Alloy Phase	Plating Deposit g/m ²	Film Forming Method	Film Deposit mg/m ²	Fe/Fe+Ni Content in Film	Oxygen Content wt. %	
156	10	δ 1	60	B	200	0.2	0.0	Comparative Example
157	10	δ 1	60	B	200	0.2	0.2	Example
158	10	δ 1	60	B	200	0.2	0.4	Example
159	10	δ 1	60	B	200	0.2	0.5	Example
160	10	δ 1	60	B	200	0.2	1.5	Example
161	10	δ 1	60	B	200	0.2	2	Example
162	10	δ 1	60	B	200	0.2	4	Example
163	10	δ 1	60	B	200	0.2	5	Example
164	10	δ 1	60	B	200	0.2	6	Example
165	10	δ 1	60	B	200	0.2	8	Example
166	10	δ 1	60	B	200	0.2	10	Example
167	10	δ 1	60	B	200	0.2	11	Example
168	10	δ 1	60	B	200	0.2	22	Example

Table 47

Specimen No.	Alloyed Zinc Dip-Plated Layer			Fe-Ni-O Film				
	Fe Content wt. %	Surface Alloy Phase	Plating Deposit g/m ²	Film Forming Method	Film Deposit mg/m ²	Fe/Fe+Ni Content in Film	Oxygen Content wt. %	
169	10	δ 1	60	C	0	0.2	1	Comparative Example
170	10	δ 1	60	C	5	0.2	1	Example
171	10	δ 1	60	C	8	0.2	1	Example
172	10	δ 1	60	C	10	0.2	1	Example
173	10	δ 1	60	C	30	0.2	1	Example
174	10	δ 1	60	C	50	0.2	1	Example
175	10	δ 1	60	C	100	0.2	1	Example
176	10	δ 1	60	C	200	0.2	1	Example
177	10	δ 1	60	C	300	0.2	1	Example
178	10	δ 1	60	C	400	0.2	1	Example
179	10	δ 1	60	C	500	0.2	1	Example
180	10	δ 1	60	C	600	0.2	1	Example
181	10	δ 1	60	C	800	0.2	1	Example
182	10	δ 1	60	C	1000	0.2	1	Example
183	10	δ 1	60	C	1200	0.2	1	Example
184	10	δ 1	60	C	1500	0.2	1	Example
185	10	δ 1	60	C	1600	0.2	1	Example
186	10	δ 1	60	C	200	0.2	0.0	Comparative Example
187	10	δ 1	60	C	200	0.2	0.2	Example
188	10	δ 1	60	C	200	0.2	0.4	Example
189	10	δ 1	60	C	200	0.2	0.5	Example
190	10	δ 1	60	C	200	0.2	1.5	Example
191	10	δ 1	60	C	200	0.2	2	Example
192	10	δ 1	60	C	200	0.2	4	Example
193	10	δ 1	60	C	200	0.2	5	Example
194	10	δ 1	60	C	200	0.2	6	Example
195	10	δ 1	60	C	200	0.2	8	Example
196	10	δ 1	60	C	200	0.2	10	Example
197	10	δ 1	60	C	200	0.2	11	Example
198	10	δ 1	60	C	200	0.2	22	Example

The measuring methods were indicated below in connection with the coating weight of a Fe-Ni-O film, the Fe/(Fe + Ni) in the film and the content of oxygen in each of the specimens.

[Coating weight of Fe-Ni-O Film and Fe/(Fe + Ni) in Film]

For quantitative analysis of a Fe-Ni-O film, the ICP method makes it difficult to completely separate the components of the Fe-Ni-O film as an overcoat from those of a plating layer as an undercoat. Thus, quantitative analysis based on the ICP method was performed to check those elements which were contained in the Fe-Ni-O film, but not contained in the undercoat or plating layer. Moreover, after sputtering of Ar ions, the XPS method was used to repetitively measure each component element in the Fe-Ni-O film from its surface so that a composition distribution of each component element was determined with respect to the depth of the plating layer. In this measuring method, the thickness of the Fe-Ni-O film was defined as $(x + (y - x)/2)$ which was calculated from adding, to the depth (defined as x) extending from a surface at which the element present in the Fe-Ni-O film but absent in the plating layer shows its maximal concentration, the difference $(y - x)$ between the depth (defined as y) extending from a surface at which the element could no longer be inspected and the first-mentioned depth (x), and then from dividing the resultant sum by 2; more specifically, as $[(x + y)/2]$ which was taken to mean an average depth of the first-mentioned depth (x) and the last-mentioned depth (y). The coating weight and composition of the Fe-Ni-O film were computed from both of the results obtained by the ICP and XPS methods, and the Fe/(Fe + Ni) in the film was then computed.

[Content of Oxygen in Film]

The content of oxygen in the film was determined from analysis of film depths by auge electron spectroscopy (AES).

Subsequently, performance evaluation was made of the above specimens for press formability, powdering resistance, spot weldability, adhesiveness and chemical treatability. Their respective testing methods were the same as in the first test.

The results of the second test are listed in Tables 48 - 57.

Table 48

Specimen No.	Press Formability		Powdering Resistance Film Peeling g/m ²	Spot Weldability Continuous Spotting	Weldability Peeling Strength kgf/25mm	Chemical Treatment	
	Friction Coefficient	Percentage Change of Outer Diameter %				State of Film Crystal	
41	0.130	8.01	6.45	7000	8.0	0	Comparative Example
42	0.126	8.33	6.25	7000	10.0	0	Example
43	0.120	8.27	5.99	7000	12.0	0	Example
44	0.125	8.34	6.30	7000	12.1	0	Example
45	0.123	8.30	5.96	7000	12.1	0	Example
46	0.126	8.49	5.74	7000	12.1	0	Example
47	0.125	8.33	5.94	7000	12.2	0	Example
48	0.118	8.20	6.01	7000	12.1	0	Example
49	0.120	8.26	6.11	7000	12.3	0	Example
50	0.125	8.13	5.76	6500	12.5	0	Example
51	0.123	8.36	6.02	6500	12.5	0	Example
52	0.122	8.46	6.21	6500	12.5	0	Example
53	0.127	8.12	5.84	6500	12.5	0	Example
54	0.124	8.45	6.12	6500	12.5	0	Example
55	0.123	8.11	5.17	6500	12.5	0	Example
56	0.121	8.06	5.03	6500	12.5	0	Example
57	0.118	8.27	6.34	6000	12.5	0	Example
58	0.125	8.14	5.92	6000	12.5	0	Example
59	0.127	8.49	6.13	5500	12.5	0	Example
60	0.125	8.03	5.75	5500	12.5	0	Example
61	0.124	8.47	6.07	5000	12.5	0	Example
62	0.120	8.14	6.62	4000	12.5	0	Example
63	0.123	8.24	6.62	3000	12.5	0	Comparative Example

Table 49

	Press Formability		Powdering Resistance Film Peeling g/m ²	Spot Weldability Continuous Spotting	Weldability Peeling Strength kgf/25mm	Chemical Treatment	
	Friction Coefficient	Percentage Change of Outer Diameter %				State of Film Crystal	Comparative Example
64	0.150	6.38	7.20	7000	7.0	0	Example
65	0.145	6.86	7.18	7000	8.0	0	Example
66	0.140	7.03	6.67	7000	9.0	0	Example
67	0.130	7.95	6.32	6500	12.0	0	Example
68	0.122	8.05	6.33	6500	12.5	0	Example
69	0.122	8.44	5.31	6500	12.5	0	Example
70	0.123	8.37	6.79	6500	12.5	0	Example
71	0.124	8.49	7.37	6500	12.5	0	Example
72	0.122	8.17	6.47	6500	12.5	0	Example
73	0.124	8.15	6.85	6000	12.5	0	Example
74	0.123	8.10	5.53	6000	12.5	0	Example
75	0.122	8.02	6.04	5000	11.0	X	Example
76	0.120	8.12	6.48	4000	11.0	X	Example

Table 50

Specimen No.	Press Formability		Powdering Resistance Film Peeling g/m ²	Spot Weldability Continuous Spotting	Weldability Peeling Strength kgf/25mm	Chemical Treatment	
	Friction Coefficient	Percentage Change of Outer Diameter %				State of Film Crystal	
77	0.150	6.60	7.14	7000	7.0	0	Comparative Example
78	0.145	6.81	6.83	7000	8.0	0	Example
79	0.140	7.07	6.60	7000	9.0	0	Example
80	0.130	7.90	6.32	6500	12.0	0	Example
81	0.122	8.39	6.46	6500	12.5	0	Example
82	0.122	8.23	6.32	6500	12.5	0	Example
83	0.123	8.10	6.36	6500	12.5	0	Example
84	0.124	8.44	6.18	6500	12.5	0	Example
85	0.122	8.24	6.77	6500	12.5	0	Example
86	0.124	8.20	6.48	6000	12.5	0	Example
87	0.123	8.34	6.46	6000	12.5	0	Example
88	0.122	8.47	6.21	5000	11.0	X	Example
89	0.120	8.11	6.22	4000	11.0	X	Example

Table 51

Specimen No.	Press Formability		Powdering Resistance Film Peeling g/m ²	Spot Weldability Continuous Spotting	Weldability Peeling Strength kgf/25mm	Chemical Treatment	
	Friction Coefficient	Percentage Change of Outer Diameter				State of Film Crystal	
90	0.170	4.55	7.54	3000	7.0	X	Comparative Example
91	0.150	4.76	7.27	3200	8.0	0	Example
92	0.140	5.36	7.22	4000	9.0	0	Example
93	0.130	6.28	7.24	5500	12.0	0	Example
94	0.128	7.45	6.14	6500	12.0	0	Example
95	0.127	7.98	6.85	7000	12.0	0	Example
96	0.115	8.04	5.34	7000	12.5	0	Example
97	0.125	8.15	7.23	7000	12.5	0	Example
98	0.123	8.22	7.00	7000	12.5	0	Example
99	0.123	8.29	5.90	7500	12.5	0	Example
100	0.122	8.39	7.36	7500	12.4	0	Example
101	0.122	8.54	6.37	8000	12.4	0	Example
102	0.122	8.56	5.31	8000	12.4	0	Example
103	0.121	8.79	5.21	8000	12.2	0	Example
104	0.121	9.03	5.99	8000	12.0	0	Example
105	0.120	9.16	6.31	8500	11.5	0	Example
106	0.120	9.17	6.55	9000	8.0	0	Example

Table 52

	Press Formability		Powdering Resistance Film Peeling g/m ²	Spot Weldability Continuous Spotting	Weldability Peeling Strength kgf/25mm	Chemical Treatment	
	Friction Coefficient	Percentage Change of Outer Diameter %				State of Film Crystal	
107	0.150	6.51	7.25	7000	7.0	0	Comparative Example
108	0.145	6.81	7.34	7000	8.0	0	Example
109	0.140	7.02	6.55	7000	9.0	0	Example
110	0.130	7.95	6.59	6500	12.0	0	Example
111	0.122	8.19	6.43	6500	12.5	0	Example
112	0.122	8.02	6.42	6500	12.5	0	Example
113	0.123	8.37	6.36	6500	12.5	0	Example
114	0.124	8.36	6.44	6500	12.5	0	Example
115	0.122	8.40	6.28	6500	12.5	0	Example
116	0.124	8.20	6.37	6000	12.5	0	Example
117	0.123	8.18	6.08	6000	12.5	0	Example
118	0.122	8.47	6.57	5000	11.0	x	Example
119	0.120	8.32	6.27	4000	11.0	x	Example

Table 53

Specimen No.	Press Formability		Powdering Resistance Film Peeling g/m ²	Spot Weldability Continuous Spotting	Weldability Peeling Strength kgf/25mm.	Chemical Treatment	
	Friction Coefficient	Percentage Change of Outer Diameter %				State of Film Crystal	
120	0.130	8.65	7.90	7000	8.0	0	Comparative Example
121	0.126	8.83	7.10	7000	10.0	0	Example
122	0.120	8.83	7.78	7000	12.0	0	Example
123	0.125	9.91	7.71	7000	12.1	0	Example
124	0.123	9.56	7.75	7000	12.1	0	Example
125	0.126	8.51	7.32	7000	12.1	0	Example
126	0.125	8.25	7.03	7000	12.2	0	Example
127	0.118	8.33	7.11	7000	12.1	0	Example
128	0.120	8.24	6.92	7000	12.3	0	Example
129	0.125	9.31	7.34	6500	12.5	0	Example
130	0.123	10.03	7.12	6500	12.5	0	Example
131	0.122	8.78	7.63	6500	12.5	0	Example
132	0.127	9.50	7.42	6500	12.5	0	Example
133	0.124	9.49	7.03	6500	12.5	0	Example
134	0.123	9.68	7.39	6500	12.5	0	Example
135	0.121	8.99	7.43	6500	12.5	0	Example
136	0.118	8.76	7.27	6000	12.5	0	Example
137	0.125	8.72	7.31	6000	12.5	0	Example
138	0.127	8.45	6.94	5500	12.5	0	Example
139	0.125	8.38	7.32	5500	12.5	0	Example
140	0.124	8.86	7.77	5000	12.5	0	Example
141	0.120	9.26	7.38	4000	12.5	0	Example
142	0.123	9.75	7.38	3000	12.5	0	Comparative Example

Table 54

	Press Formability		Powdering Resistance Film Peeling g/m ²	Spot Weldability Continuous Spotting	Weldability Peeling Strength kgf/25mm	Chemical Treatment	
	Friction Coefficient	Percentage Change of Outer Diameter %				State of Film Crystal	Comparative Example
143	0.150	6.38	8.82	7000	7.0	0	Example
144	0.145	6.58	8.89	7000	8.0	0	Example
145	0.140	6.66	8.24	7000	9.0	0	Example
146	0.130	7.07	7.85	6500	12.0	0	Example
147	0.122	8.53	7.36	6500	12.5	0	Example
148	0.122	8.81	7.24	6500	12.5	0	Example
149	0.123	9.73	7.10	6500	12.5	0	Example
150	0.124	8.51	7.10	6500	12.5	0	Example
151	0.122	8.98	7.32	6500	12.5	0	Example
152	0.124	9.87	7.54	6000	12.5	0	Example
153	0.123	9.01	6.98	6000	12.5	0	Example
154	0.122	8.42	7.01	5000	11.0	X	Example
155	0.120	9.21	7.33	4000	11.0	X	Example

Table 55

Specimen No.	Press Formability		Powdering Resistance Film Peeling g/m ²	Spot Weldability Continuous Spotting	Weldability Peeling Strength kgf/25mm	Chemical Treatment	
	Friction Coefficient	Percentage Change of Outer Diameter %				State of Film Crystal	
156	0.150	5.66	8.79	7000	7.0	0	Comparative Example
157	0.145	6.01	8.64	7000	8.0	0	Example
158	0.140	6.44	8.13	7000	9.0	0	Example
159	0.130	7.73	8.15	6500	12.0	0	Example
160	0.122	9.47	7.60	6500	12.5	0	Example
161	0.122	8.05	7.16	6500	12.5	0	Example
162	0.123	8.61	7.19	6500	12.5	0	Example
163	0.124	8.86	6.70	6500	12.5	0	Example
164	0.122	9.55	6.94	6500	12.5	0	Example
165	0.124	9.99	7.33	6000	12.5	0	Example
166	0.123	9.75	6.90	6000	12.5	0	Example
167	0.122	8.68	6.83	5000	11.0	X	Example
168	0.120	8.96	6.94	4000	11.0	X	Example

Table 56

Specimen No.	Press Formability		Powdering Resistance Film Peeling g/m ²	Spot Weldability Continuous Spotting	Weldability Peeling Strength kgf/25mm	Chemical Treatment	
	Friction Coefficient	Percentage Change of Outer Diameter %				State of Film Crystal	
169	0.170	5.07	9.17	3000	7.0	X	Comparative Example
170	0.150	5.19	8.99	3200	8.0	0	Example
171	0.140	5.21	8.74	4000	9.0	0	Example
172	0.130	6.00	8.46	5500	12.0	0	Example
173	0.128	7.22	7.77	6500	12.0	0	Example
174	0.127	7.77	7.64	7000	12.0	0	Example
175	0.115	8.49	7.88	7000	12.5	0	Example
176	0.125	8.62	7.36	7000	12.5	0	Example
177	0.123	8.99	7.80	7000	12.5	0	Example
178	0.123	9.81	7.49	7500	12.5	0	Example
179	0.122	9.87	7.10	7500	12.4	0	Example
180	0.122	10.79	7.01	8000	12.4	0	Example
181	0.122	11.07	6.84	8000	12.4	0	Example
182	0.121	11.13	6.73	8000	12.2	0	Example
183	0.121	11.13	7.13	8000	12.0	0	Example
184	0.120	11.67	7.30	8500	11.5	0	Example
185	0.120	11.95	7.26	9000	8.0	0	Example

Table 57

	Press Formability		Powdering Resistance Film Peeling g/m ²	Spot Weldability Continuous Spotting	Weldability Peeling Strength kgf/25mm	Chemical Treatment	
	Friction Coefficient	Percentage Change of Outer Diameter %				State of Film Crystal	
186	0.150	5.84	9.07	7000	7.0	0	Comparative Example
187	0.145	6.43	8.87	7000	8.0	0	Example
188	0.140	7.35	8.11	7000	9.0	0	Example
189	0.130	8.33	7.91	6500	12.0	0	Example
190	0.122	9.29	7.27	6500	12.5	0	Example
191	0.122	8.74	7.26	6500	12.5	0	Example
192	0.123	9.85	6.99	6500	12.5	0	Example
193	0.124	8.90	7.29	6500	12.5	0	Example
194	0.122	8.35	6.90	6500	12.5	0	Example
195	0.124	8.91	7.01	6000	12.5	0	Example
196	0.123	8.91	7.27	6000	12.5	0	Example
197	0.122	8.89	7.23	5000	11.0	X	Example
198	0.120	9.67	7.09	4000	11.0	X	Example

As is evident from the results of Tables 48 - 57, various facets have been found which are similar to those obtained in the first test. As for press formability, powdering resistance, spot weldability and adhesiveness, the inventive specimens have also proved clearly distinct from the comparative specimens. The following facts have been further elucidated.

Coating weights of the Fe-Ni-O film falling within the scope of the present invention lead to higher press formability as the coating weight lies far to an upper limit. Less than 10 mg/m² of the Fe-Ni-O film as an overcoat is less effective to improve press formability, and more than 1500 mg/m² produces no better results in improving such physical property.

Coating weights of the Fe-Ni-O film within the scope of the invention are conducive to higher spot weldability as the coating weight is greater.

If Fe/(Fe + Ni) in the Fe-Ni-O film is below 0.004 wt. %, then no sufficient improvement in adhesiveness is attainable. Conversely, if Fe/(Fe + Ni) exceeds 0.9 wt. %, the content of Ni in that film becomes small, failing to improve spot weldability.

Below 0.5 wt. % in the content of oxygen in the Fe-Ni-O film fails to adequately improve press formability and spot weldability. Above 10 wt. % deteriorates chemical treatability.

Because the present invention is constructed as noted and specified hereinabove, a Fe-Ni-O film formed on a plating layer of an alloyed zinc dip-plated steel sheet is rigid in nature and high in melting point as compared to a zinc- or zinc alloy-plating layer. This means that when the alloyed zinc dip-plated steel sheet is press molded, sliding resistance is reduced between the plating layer and the mating pressure mold with eventual easy flowing of the steel sheet into the mold. Furthermore, the presence of the Fe-Ni-O film, especially the content of Ni in a specified amount, ensures that the ratio of a high-melting Zn-Ni alloy to be formed be held at a desired level when in welding; and hence, wasted electrode be prevented, and continuous spot-weldability be improved in the case of spot welding. Also advantageously, Fe is contained in a specified amount, which element is capable of generating high surface potential suited for improving adhesiveness so that an adhesive-bonded plate is obtainable with enhanced peeloff strength. To add to those advantages, chemical treatability causes Ni and Fe of the Fe-Ni-O film to incorporate into a phosphate crystal, ultimately producing high adhesiveness and also forming a dense, uniform phosphate crystal, hence excellent secondary adhesiveness in warm water.

In consequence, the present invention provides an alloyed zinc dip-plated steel sheet which is highly satisfactory in respect of press formability, spot weldability, adhesiveness and chemical treatability, and industrially useful with significant benefits.

Claims

1. A method for manufacturing a zinciferous plated steel sheet, comprising the steps of:

forming a zinciferous plating layer on a steel sheet;
and
forming an Fe-Ni-O film on the zinciferous plating layer.

2. The method of claim 1, wherein said step of forming the Fe-Ni-O film comprises carrying out electrolysis with the steel sheet, on which the zinciferous plating layer is formed, as a cathode in an aqueous solution containing nickel sulfate, ferrous sulfate and ferric sulfate; and

said aqueous solution has a total concentration of the nickel sulfate, the ferrous sulfate and the ferric sulfate, a ratio of concentration (mol/l) of an Fe³⁺ to a sum of concentration of an Fe²⁺ and the Fe³⁺ and a pH, said total concentration is within a range of from 0.3 to 2 mol/l, said ratio of concentration (mol/l) is within a range of from 0.5 to less than 1.0, and a pH is within a range of from 1 to 2.

3. The method of claim 1, wherein said zinciferous plating layer is an alloyed zinc dip-plating layer having an iron content within a range of from 7 to 15 wt. %.

4. The method of claim 1, wherein said zinciferous plating layer is a zinc electroplating layer.

5. The method of claim 1, wherein said zinciferous plating layer is a zinc dip-plating layer.

6. The method of claim 1, wherein said step of forming the Fe-Ni-O film comprises carrying out electrolysis with the steel sheet, on which the zinciferous plating layer is formed, as a cathode in a plating solution containing nickel sulfate and ferrous sulfate; and

said plating solution has a total concentration of the nickel sulfate and the ferrous sulfate and a pH, the total concentration is within a range of from 0.1 to 2 mol/l and the pH is within a range of from 1 to 3; and

the electrolysis is carried out on conditions satisfying the following equation:

$$50 \leq I_K / (U^{1/2} \cdot M) \leq 150$$

where

M represents a sum of the concentrations (mol/l) of nickel ions and ferrous ions in the plating solution;

U represents a mean flow rate (m/s) of the plating solution; and

i_k represents a current density (A/dm²) in the electrolysis.

- 5 7. The method of claim 6, wherein said zinciferous plating layer is an alloyed zinc dip-plating layer having an iron content within a range of from 7 to 15 wt.%.
8. The method of claim 6, wherein said zinciferous plating layer is a zinc electroplating layer.
- 10 9. The method of claim 6, wherein said zinciferous plating layer is a zinc dip-plating layer.
10. The method of claim 1, wherein said step of forming the Fe-Ni-O film comprises dipping the steel sheet, on which the zinciferous plating layer is formed, in an aqueous solution containing at least one of ferrous sulfate and ferrous nitrate and at least one of nickel sulfate and nickel nitrate; and
 - 15 a sum of an iron content (mol/l) and a nickel content (mol/l) in the aqueous solution is within a range of from 0.1 to 3.0 mol/l, a ratio of the iron content (mol/l) to the sum of the iron content (mol/l) and the nickel content (mol/l) in the aqueous solution is within a range of from 0.004 to 0.9, pH is within a range of from 1.0 to 3.5, and temperature is within a range of from 20 to 70 °C.
- 20 11. The method of claim 1, after the step of forming a zinciferous plating layer on the steel sheet and before the step of forming an Fe-Ni-O film on the zinciferous plating layer, further comprising the step of treating the steel sheet, on which the zinciferous plating layer is formed, in an alkaline solution having a pH of at least 10 for a period within a range of from 2 to 30 seconds.
- 25 12. The method of claim 11, wherein said step of forming the Fe-Ni-O film comprises treating the steel sheet, on which the zinciferous plating layer is formed, in an aqueous solution containing FeCl₂ and NiCl₂ and having a pH within a range of from 2.0 to 3.5 and a temperature within a range of from 20 to 70 °C.
- 30 13. The method of claim 11, wherein said step of forming the Fe-Ni-O film comprises treating the steel sheet, on which the zinciferous plating layer is formed, in an aqueous solution containing FeCl₂ and NiCl₂ and having a pH within a range of from 2.0 to 3.5, a temperature within a range of from 20 to 70 °C, and a ratio of Fe content (wt.%) to the sum of the Fe content (wt.%) and a Ni content (wt.%) being within a range of from 0.004 to 0.9.
- 35 14. The method of claim 1, wherein said step of forming the Fe-Ni-O film comprises:
 - spraying a mist solution containing Fe ions and Ni ions and having pH of 1 to 3.5 on a surface of the zinciferous plating layer which is formed on the steel sheet;
 - maintaining the steel sheet at a temperature of 20 to 70 °C for 1 second or more; and
 - heating the steel sheet;
 - 40 thereby the Fe-Ni-O film having a coating weight within the range of 10 to 1500 mg/m² in terms of the total weight of the metallic elements, a rate of coating within the range of 30 to 90%, and an island-like or mosaic distribution being formed on the zinciferous plating layer.
- 45 15. The method of claim 14, wherein said mist solution has a ratio of a Fe content (g/l) to the total of the Fe content (g/l) and a Ni content (g/l) and said ratio is 0.004 to 0.9.
16. The method of claim 14, wherein said heating of the zinciferous plated steel sheet is carried out at a temperature of 80 to 500 °C.
- 50 17. The method of claim 1, wherein said step of forming the Fe-Ni-O film comprises:
 - temper rolling the steel sheet, on which the zinciferous plating layer is formed, to form fine irregularities on the zinciferous plating layer; and
 - forming the Fe-Ni-O film on the zinciferous plating layer,
 - 55 thereby the Fe-Ni-O film having a coating weight within the range of 10 to 1500 mg/m² in terms of the total weight of the metallic elements, a rate of coating within the range of 30 to 90%, and an island-like or mosaic distribution being formed on the zinciferous plating layer.
18. The method of claim 17, wherein the Fe-Ni-O film is formed by anodic electrolysis using the electrolytic solution

containing nickel sulfate, ferrous sulfate and ferric sulfate in a total amount of 0.3 to 2.0 mol/l, and having a pH of 1 to 2.

19. The method of claim 18, wherein said electrolytic solution satisfies the conditions that a ratio of a Fe content (g/l) to the total of the Fe content (g/l) and a Ni content (g/l) is within the range of 0.004 to 0.9, and a molar ratio of ferrous sulfate (mol/l) to the total of the ferrous sulfate (mol/l) and ferric sulfate (mol/l) is 0.5 to less than 1.0.

20. The method of claim 17, wherein said step of forming the Fe-Ni-O film comprises treating the steel sheet, on which the zinciferous plating layer is formed, by using an aqueous solution, the aqueous solution containing FeCl_2 and NiCl_2 , and satisfying the conditions that the pH is 2.0 to 3.5, and the temperature is 20 to 70 °C.

21. The method of claim 17, wherein said step of forming the Fe-Ni-O film comprises treating the steel sheet, on which the zinciferous plating layer is formed, by using an aqueous solution, the aqueous solution containing FeCl_2 and NiCl_2 , and satisfying the conditions that a ratio of a Fe content (g/l) to the total of the Fe content (g/l) and a Ni content (g/l) is 0.004 to 0.9, a pH is 2.0 to 3.5, and the temperature is 20 to 70 °C.

22. The method of claim 1, wherein said step of forming the Fe-Ni-O film comprises:

temper rolling the steel sheet, on which the zinciferous plating layer is formed, to form a new surface on the zinciferous plating layer; and forming the Fe-Ni-O film on the zinciferous plating layer, thereby the Fe-Ni-O film having a coating weight within the range of 10 to 1500 mg/m² in terms of the total weight of the metallic elements, a rate of coating within the range of 30 to 90%, and an island-like or mosaic distribution being formed on the zinciferous plating layer.

23. The method of claim 22, wherein the Fe-Ni-O film is formed by anodic electrolysis using the electrolytic solution containing nickel sulfate, ferrous sulfate and ferric sulfate in a total amount of 0.3 to 2.0 mol/l, and having a pH of 1 to 2.

24. The method of claim 22, wherein said electrolytic solution satisfies the conditions that a ratio of a Fe content (g/l) to the total of the Fe content (g/l) and a Ni content (g/l) is within the range of 0.004 to 0.9, and a molar ratio of ferrous sulfate (mol/l) to the total of the ferrous sulfate (mol/l) and ferric sulfate (mol/l) is 0.5 to less than 1.0.

25. The method of claim 22, wherein said step of forming the Fe-Ni-O film comprises treating the steel sheet, on which the zinciferous plating layer is formed, by using an aqueous solution, the aqueous solution containing FeCl_2 and NiCl_2 , and satisfying the conditions that the pH is 2.0 to 3.5, and the temperature is 20 to 70 °C.

26. The method of claim 22, wherein said step of forming the Fe-Ni-O film comprises treating the steel sheet, on which the zinciferous plating layer is formed, by using an aqueous solution, the aqueous solution containing FeCl_2 and NiCl_2 , and satisfying the conditions that a ratio of a Fe content (g/l) to the total of the Fe content (g/l) and a Ni content (g/l) is 0.004 to 0.9, a pH is 2.0 to 3.5, and the temperature is 20 to 70 °C.

27. The method of claim 1, wherein said step of forming the Fe-Ni-O film comprises:

dipping the steel sheet, on which the zinciferous plating layer is formed, in an acid solution or an alkaline solution to dissolve an air oxide film existing on a surface of the zinciferous plating layer and to form active and inactive portions on the surface of the zinciferous plating layer; and forming the Fe-Ni-O film on the zinciferous plating layer on which the active and inactive portions are formed, thereby the Fe-Ni-O film having a coating weight within the range of 10 to 1500 mg/m² in terms of the total weight of the metallic elements, a rate of coating within the range of 30 to 90%, and an island-like or mosaic distribution being formed on the zinciferous plating layer.

28. The method of claim 27, wherein the Fe-Ni-O film is formed by anodic electrolysis using the electrolytic solution containing nickel sulfate, ferrous sulfate and ferric sulfate in a total amount of 0.3 to 2.0 mol/l, and having a pH of 1 to 2.

29. The method of claim 28, wherein said electrolytic solution satisfies the conditions that a ratio of a Fe content (g/l) to the total of the Fe content (g/l) and a Ni content (g/l) is within the range of 0.004 to 0.9, and a molar ratio of ferrous sulfate (mol/l) to the total of the ferrous sulfate (mol/l) and ferric sulfate (mol/l) is 0.5 to less than 1.0.

30. The method of claim 27, wherein said step of forming the Fe-Ni-O film comprises treating the steel sheet, on which the zinciferous plating layer is formed, by using an aqueous solution, the aqueous solution containing FeCl_2 and NiCl_2 , and satisfying the conditions that the pH is 2.0 to 3.5, and the temperature is 20 to 70 °C.

31. The method of claim 27, wherein said step of forming the Fe-Ni-O film comprises treating the steel sheet, on which the zinciferous plating layer is formed, by using an aqueous solution, the aqueous solution containing FeCl_2 and NiCl_2 , and satisfying the conditions that a ratio of a Fe content (g/l) to the total of the Fe content (g/l) and a Ni content (g/l) is 0.004 to 0.9, a pH is 2.0 to 3.5, and the temperature is 20 to 70 °C.

32. The method of claim 1, wherein said step of forming the Fe-Ni-O film comprises:

performing an anodic electrolysis in an acid solution or an alkaline solution to the steel sheet, on which the zinciferous plating layer is formed, to dissolve an air oxide film existing on a surface of the zinciferous plating layer and to form active and inactive portions on the surface of the zinciferous plating layer; and forming the Fe-Ni-O film on the zinciferous plating layer on which the active and inactive portions are formed, thereby the Fe-Ni-O film having a coating weight within the range of 10 to 1500 mg/m² in terms of the total weight of the metallic elements, a rate of coating within the range of 30 to 90%, and an island-like or mosaic distribution being formed on the zinciferous plating layer.

33. The method of claim 32, wherein the Fe-Ni-O film is formed by anodic electrolysis using the electrolytic solution containing nickel sulfate, ferrous sulfate and ferric sulfate in a total amount of 0.3 to 2.0 mol/l, and having a pH of 1 to 2.

34. The method of claim 33, wherein said electrolytic solution satisfies the conditions that a ratio of a Fe content (g/l) to the total of the Fe content (g/l) and a Ni content (g/l) is within the range of 0.004 to 0.9, and a molar ratio of ferrous sulfate (mol/l) to the total of the ferrous sulfate (mol/l) and ferric sulfate (mol/l) is 0.5 to less than 1.0.

35. The method of claim 32, wherein said step of forming the Fe-Ni-O film comprises treating the steel sheet, on which the zinciferous plating layer is formed, by using an aqueous solution, the aqueous solution containing FeCl_2 and NiCl_2 , and satisfying the conditions that the pH is 2.0 to 3.5, and the temperature is 20 to 70 °C.

36. The method of claim 32, wherein said step of forming the Fe-Ni-O film comprises treating the steel sheet, on which the zinciferous plating layer is formed, by using an aqueous solution, the aqueous solution containing FeCl_2 and NiCl_2 , and satisfying the conditions that a ratio of a Fe content (g/l) to the total of the Fe content (g/l) and a Ni content (g/l) is 0.004 to 0.9, a pH is 2.0 to 3.5, and the temperature is 20 to 70 °C.

37. The method of claim 1, wherein said step of forming the Fe-Ni-O film comprises:

temper rolling the steel sheet, on which the zinciferous plating layer is formed, within the range of an elongation ratio of 0.3 to 5.0 %; performing an alkali treatment to the temper-rolled steel sheet in an alkaline solution having a pH of 10 or more for the period of 2 to 30 seconds; and forming the Fe-Ni-O film on the surface of the zinciferous plating layer for which the alkali treatment is performed.

38. The method of claim 37, wherein said step of forming the Fe-Ni-O film comprises treating the steel sheet, on which the zinciferous plating layer is formed, by using an aqueous solution, the aqueous solution containing FeCl_2 and NiCl_2 , and having a pH of 2.0 to 3.5, and a temperature of 20 to 70 °C.

39. The method of claim 37, wherein said step of forming the Fe-Ni-O film comprises treating the steel sheet, on which the zinciferous plating layer is formed, by using an aqueous solution, the aqueous solution containing FeCl_2 and NiCl_2 , and satisfying the conditions that a ratio of a Fe content (g/l) to the total of the Fe content (g/l) and a Ni content (g/l) is 0.004 to 0.9, a pH is 2.0 to 3.5, and the temperature is 20 to 70 °C.

40. The method of claim 1, wherein said step of forming the Fe-Ni-O film comprises:

performing an alkali treatment to the steel sheet, on which the zinciferous plating layer is formed, in an alkaline solution having a pH of 10 or more for the period of 2 to 30 seconds; temper rolling the steel sheet, for which the alkali treatment is performed, within the range of an elongation ratio

of 0.3 to 5.0 %; and

forming the Fe-Ni-O film on the surface of the plating layer of the temper rolled steel sheet.

41. The method of claim 40, wherein said step of forming the Fe-Ni-O film comprises treating the steel sheet, on which the zinciferous plating layer is formed, by using an aqueous solution, the aqueous solution containing FeCl_2 and NiCl_2 , and having a pH of 2.0 to 3.5, and a temperature of 20 to 70 °C.

42. The method of claim 40, wherein said step of forming the Fe-Ni-O film comprises treating the steel sheet, on which the zinciferous plating layer is formed, by using an aqueous solution, the aqueous solution containing FeCl_2 and NiCl_2 , and satisfying the conditions that a ratio of a Fe content (g/l) to the total of the Fe content (g/l) and a Ni content (g/l) is 0.004 to 0.9, a pH is 2.0 to 3.5, and the temperature is 20 to 70 °C.

43. A zinciferous plated steel sheet comprising:

a steel sheet;

a zinciferous plating layer which is formed on the steel sheet; and

an Fe-Ni-O film which is formed on the zinciferous plating layer.

44. The zinciferous plated steel sheet of claim 43, wherein

said Fe-Ni-O film has an island-like or mosaic form;

said Fe-Ni-O film has a coating weight within the range of 10 to 1500 mg/m^2 in terms of the total weight of metallic elements in the Fe-Ni-O film; and

said Fe-Ni-O film has a rate of surface coating within the range of 30 to 90%.

45. The zinciferous plated steel sheet of claim 43, wherein

said Fe-Ni-O film has a ratio of the Fe content (wt%) to the total of the Fe content (wt%) and a Ni content (wt%) which is within the range of 0.004 to 0.9; and

said Fe-Ni-O film has an oxygen content which is within the range of 0.5 to 10 wt%.

46. The zinciferous plated steel sheet of claim 43, wherein

said zinciferous plating layer is an alloyed zinc dip-plating layer;

said alloyed zinc dip-plating layer comprises 6 to 11 wt. % Fe and the balance being Zn and inevitable; and

said alloyed zinc dip-plating layer has a coating weight of 20 to 100 g/m^2 .

47. The zinciferous plated steel sheet of claim 43, wherein

said zinciferous plating layer is an alloyed zinc dip-plating layer;

said alloyed zinc dip-plating layer comprises 9 to 14 wt. % Fe and the balance being Zn and inevitable;

said alloyed zinc dip-plating layer has a surface alloy phase which is δ 1 alloy phase; and

said alloyed zinc dip-plating layer has a coating weight of 20 to 100 g/m^2 .

48. The zinciferous plated steel sheet of claim 43, wherein

said Fe-Ni-O film has a coating weight within the range of 10 to 1500 mg/m^2 in terms of the total weight of metallic elements in the Fe-Ni-O film; and

said Fe-Ni-O film has a ratio of the Fe content (wt%) to the total of the Fe content (wt%) and a Ni content (wt%) which is within the range of 0.004 to 0.9; and

said Fe-Ni-O film has an oxygen content which is within the range of 0.5 to 10 wt%.

FIG. 1

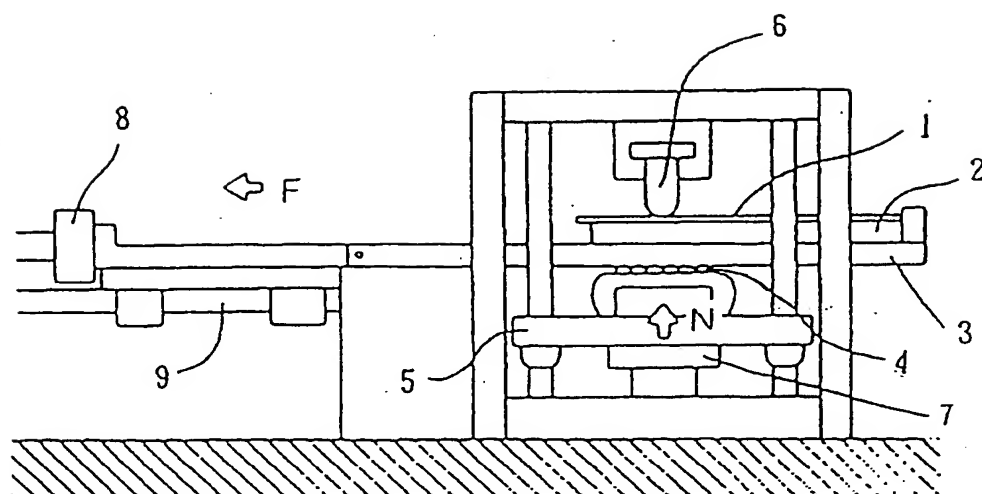


FIG. 2

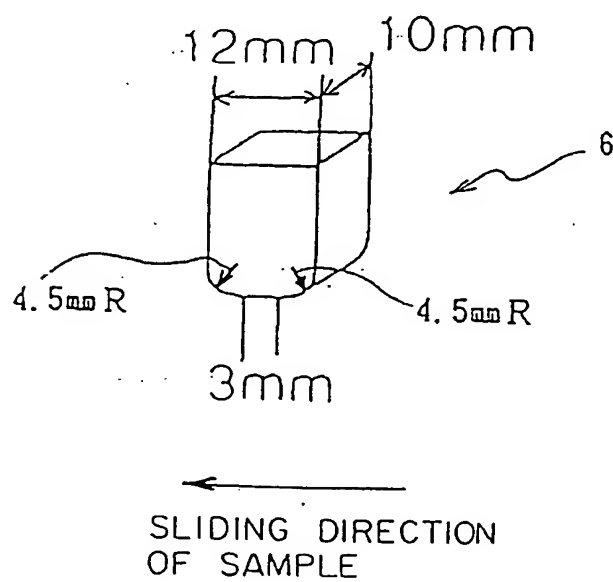


FIG. 3

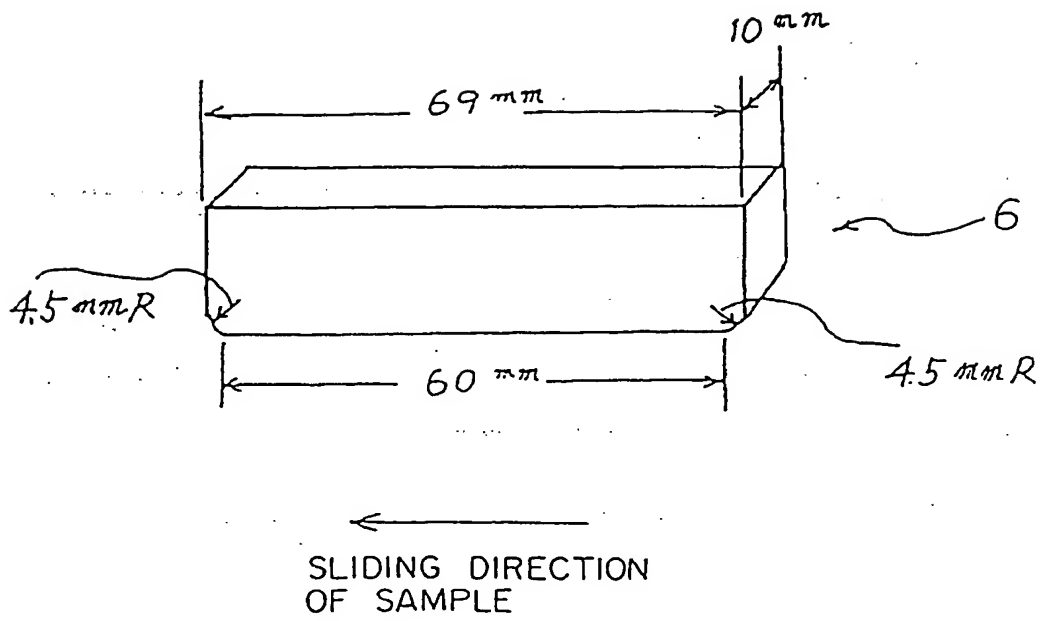


FIG. 4

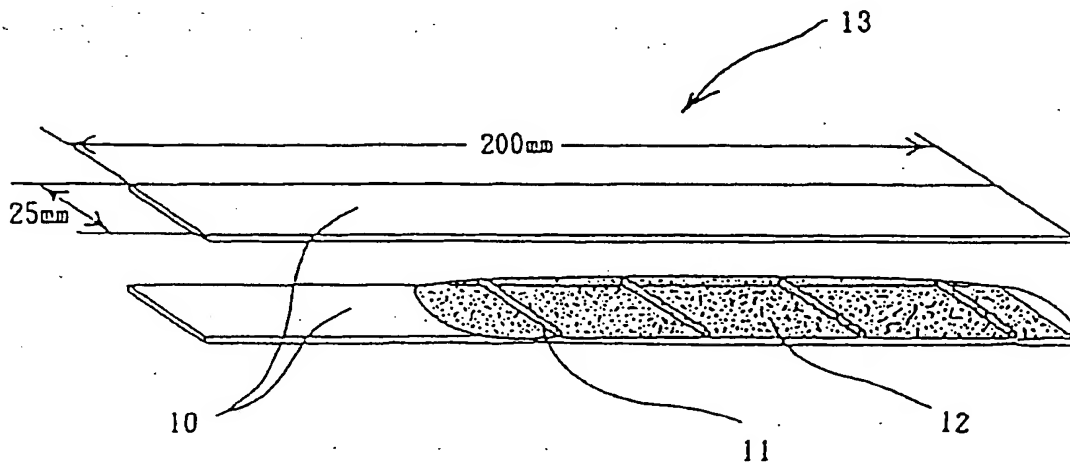


FIG. 5

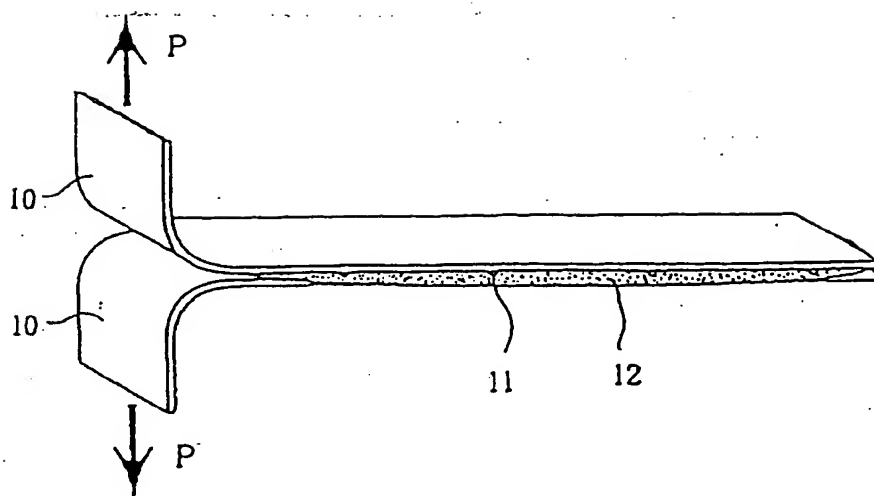


FIG. 6

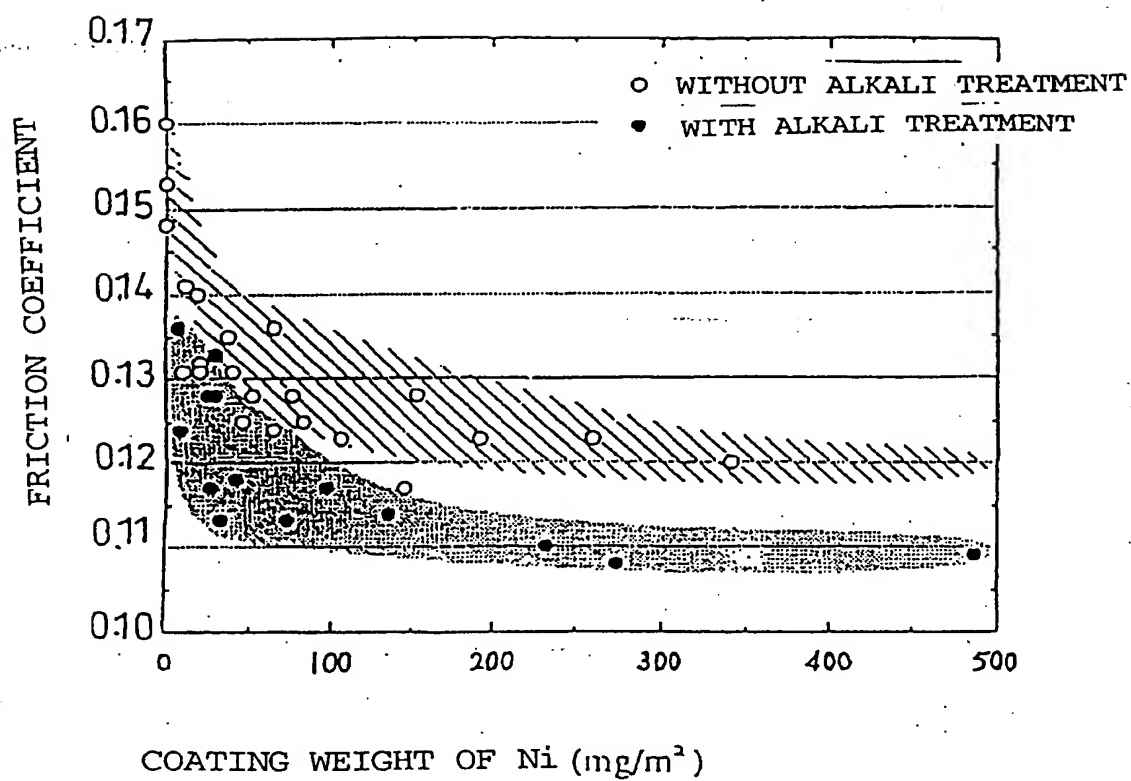


FIG. 7

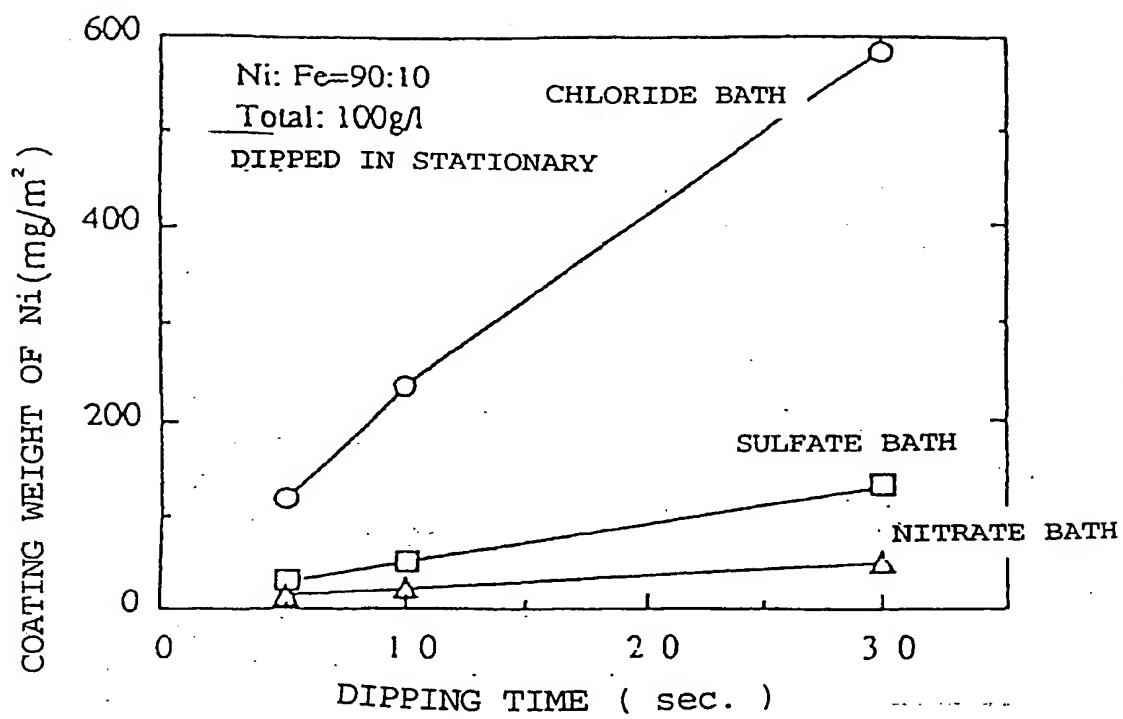


FIG. 8

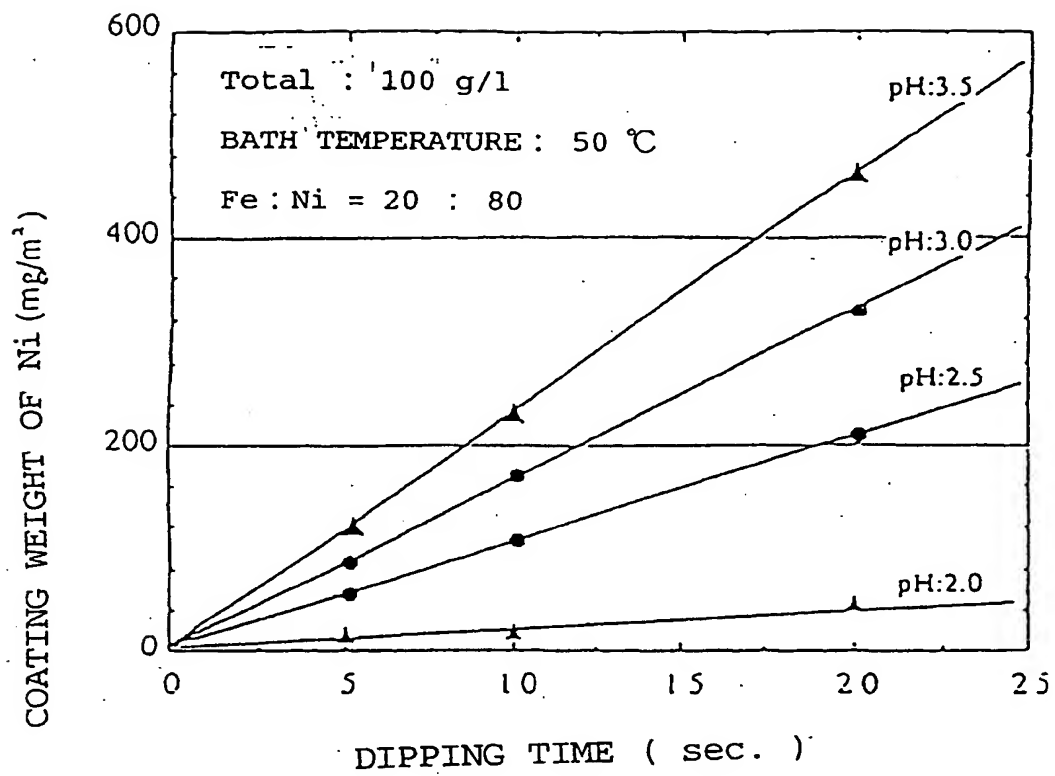


FIG. 9

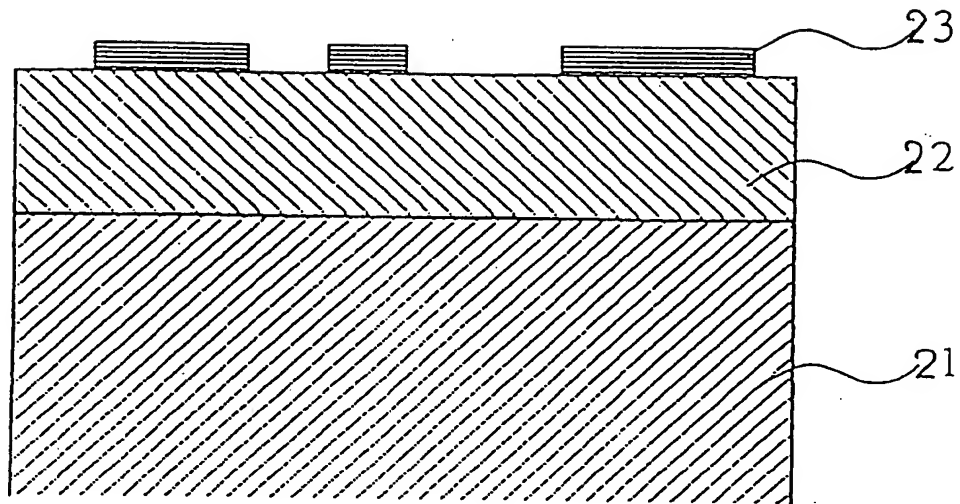


FIG. 10

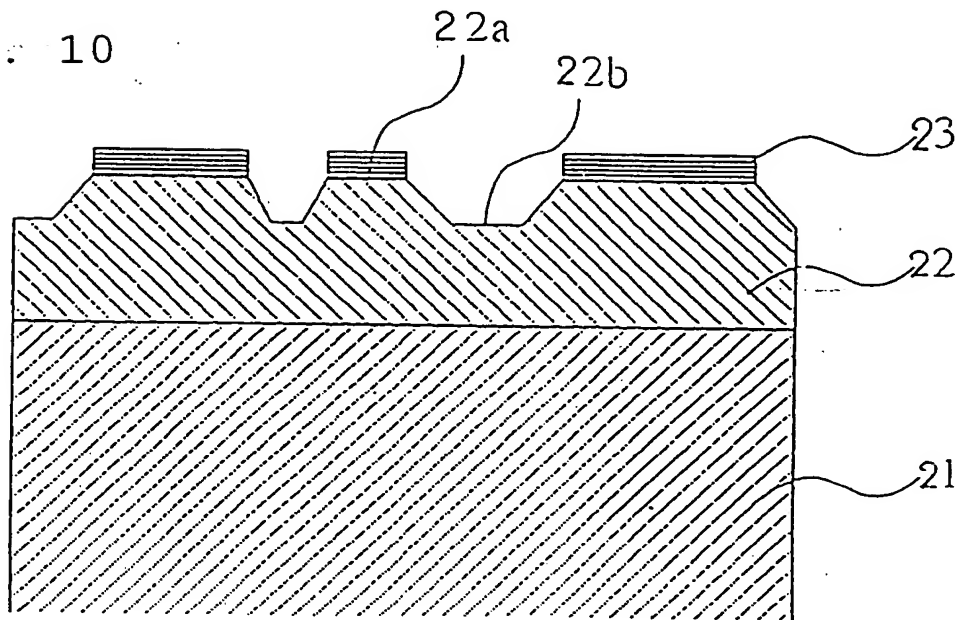


FIG. 11

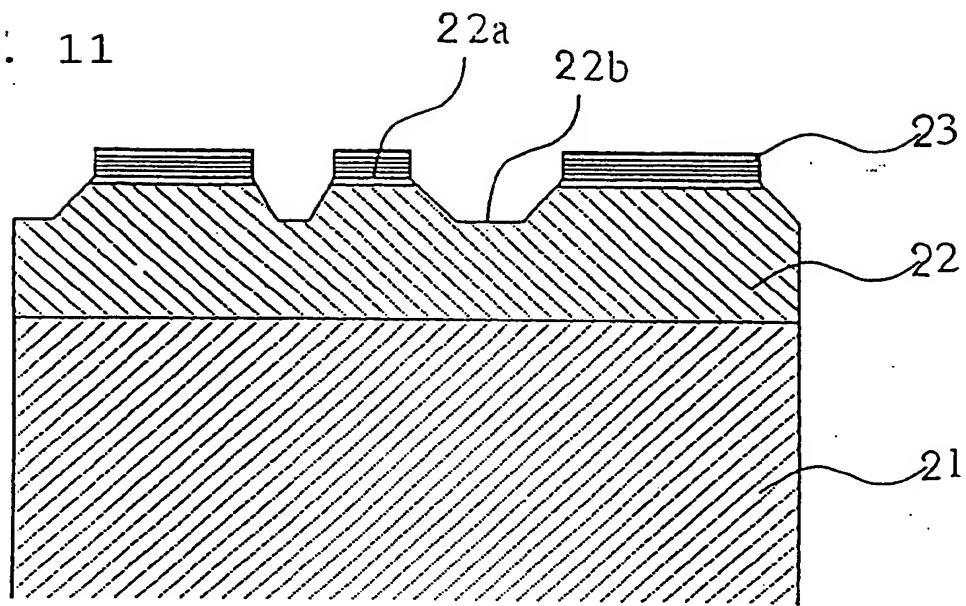


FIG. 12

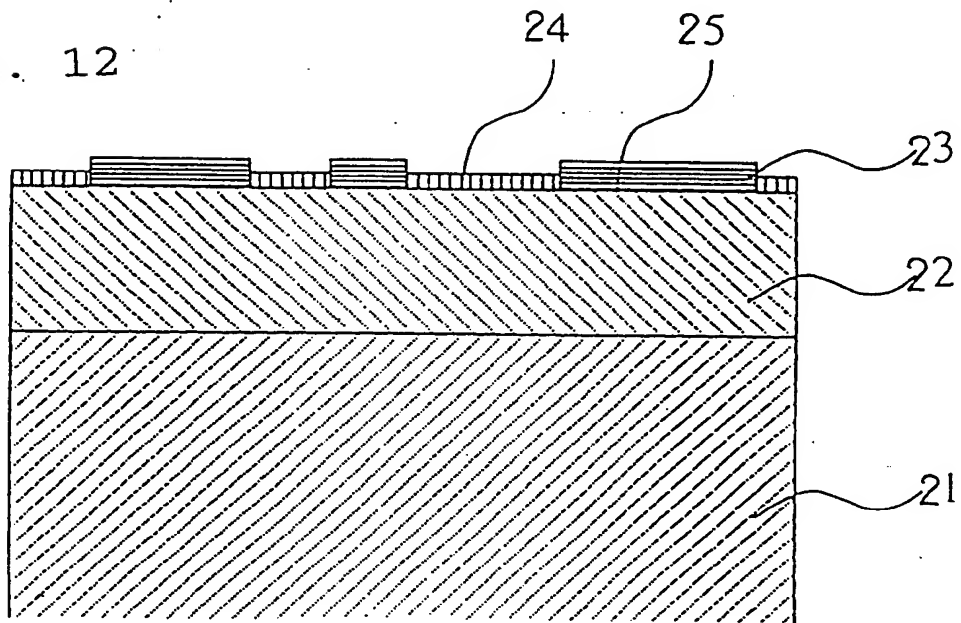


FIG. 13

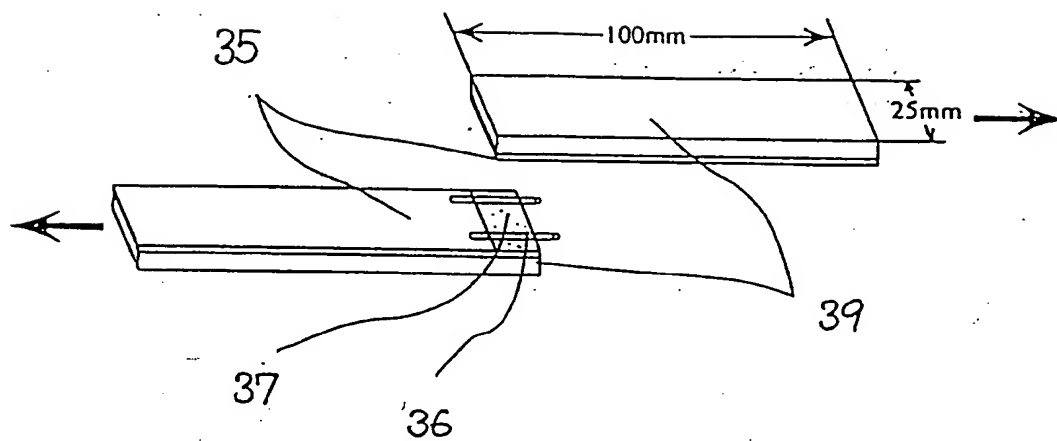


FIG. 14

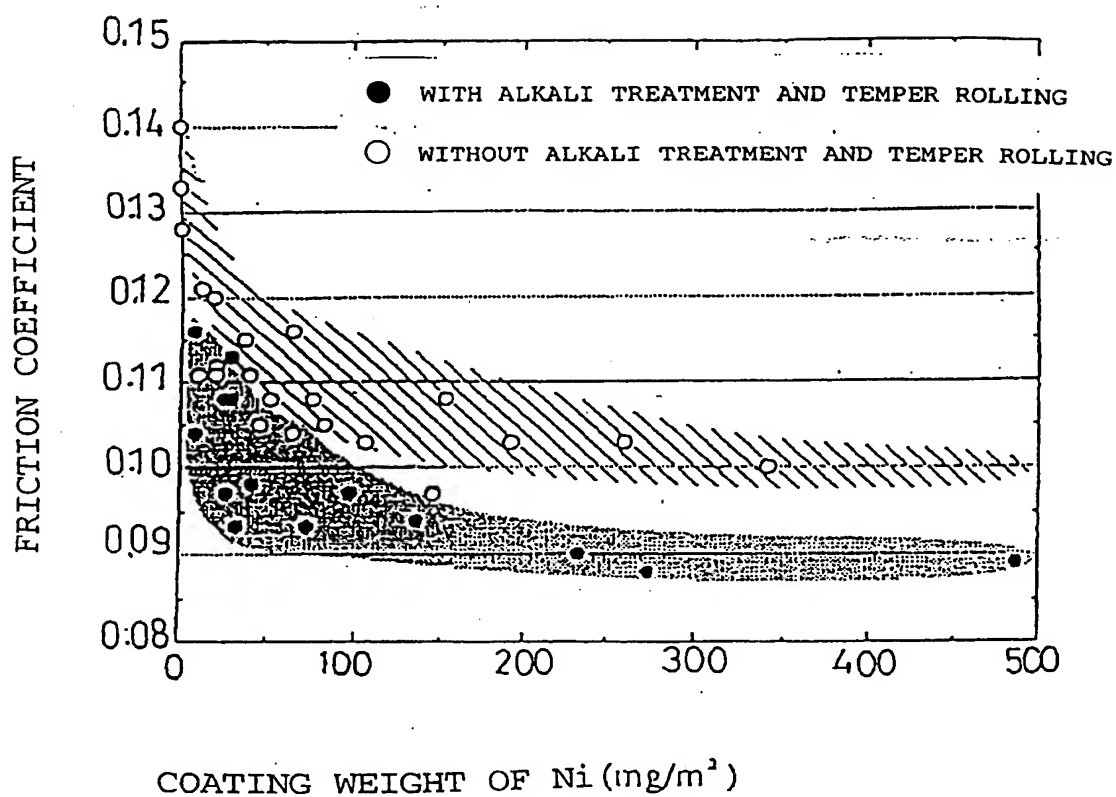


FIG. 15

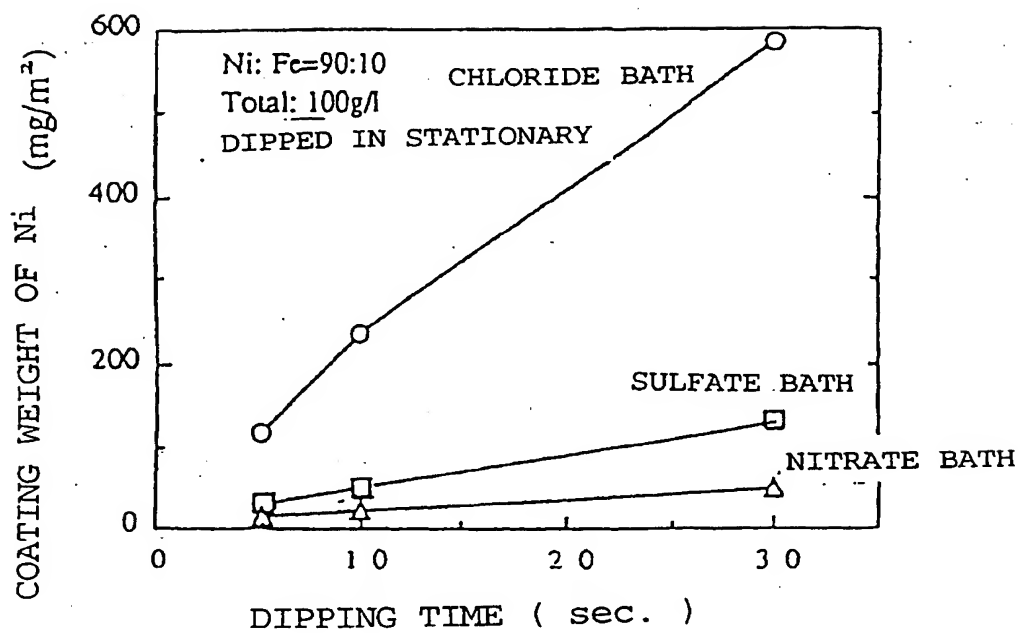


FIG. 16

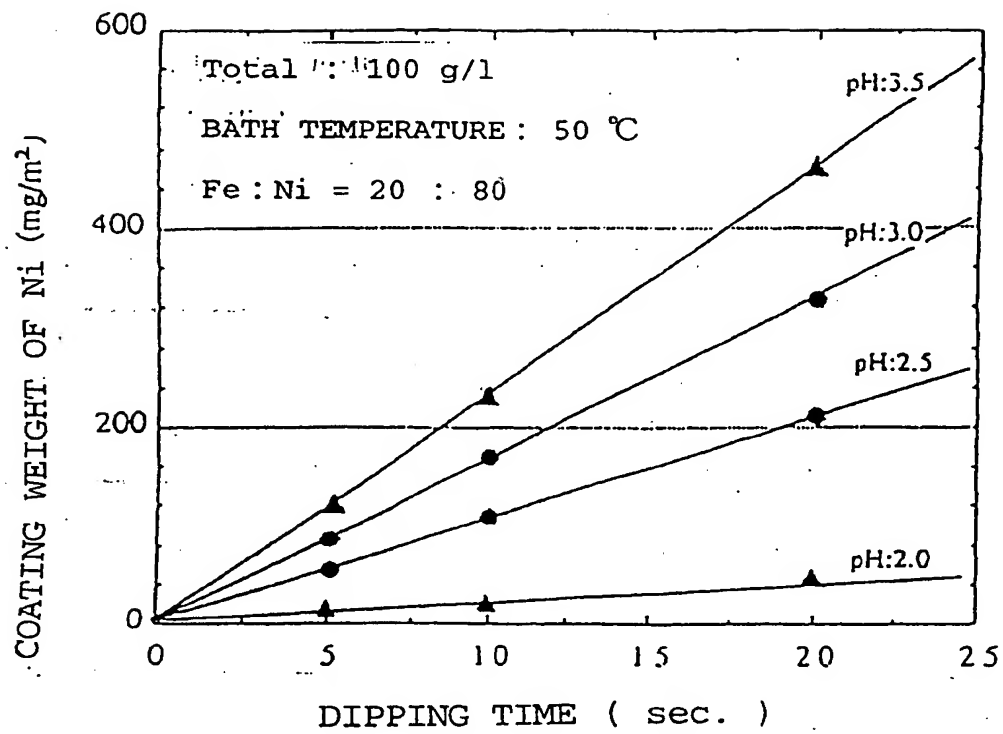


FIG. 17

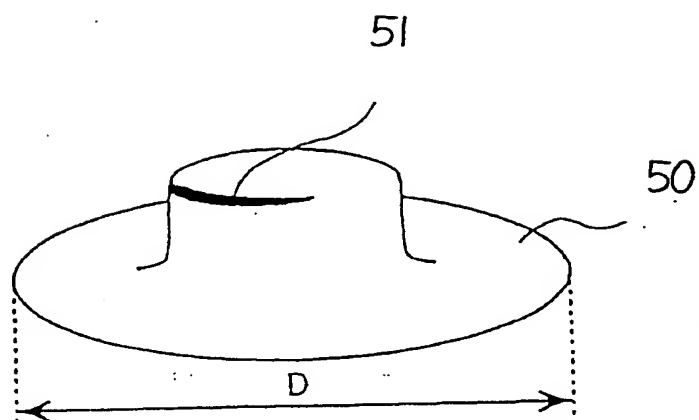


FIG. 18

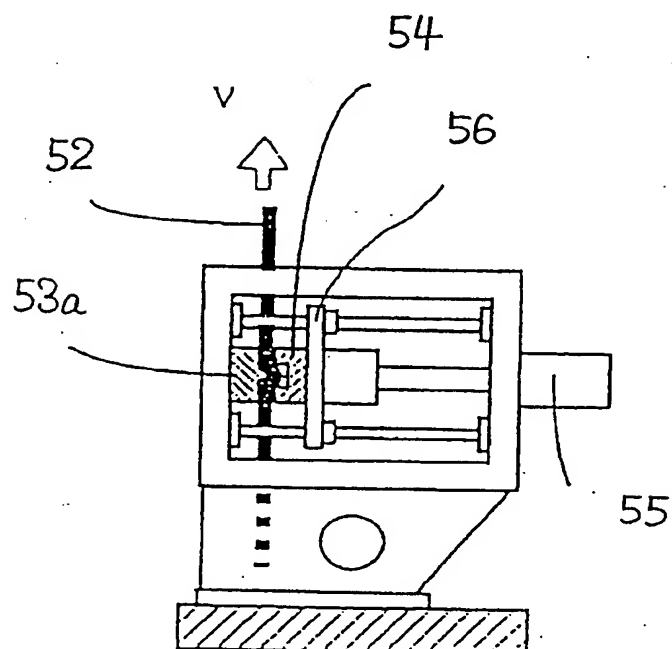


FIG. 19

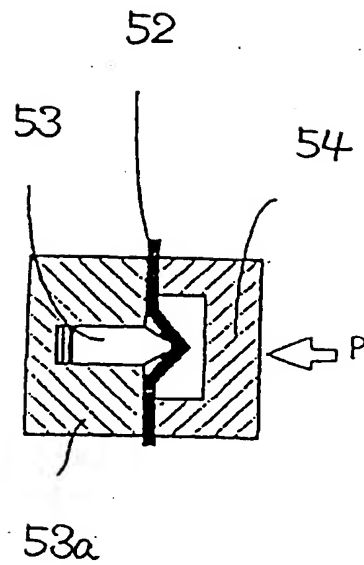


FIG. 20

